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EVALUATION OF ELECTRIC FIELD GRADIENTS
IN MOLECULES
USING SEMI - EMPIRICAL MO FORMALISMS

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
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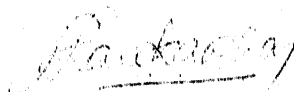
" Of making many books there is no end; and much study is a weariness of the flesh."

(Ecclesiastes 12:12)

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor P.T. Narasimhan.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.



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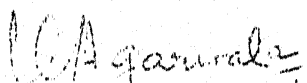
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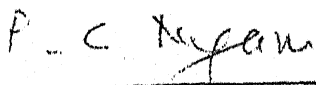
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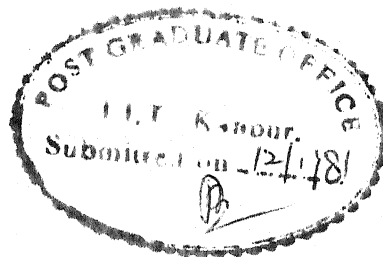
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Certified that the work contained in this thesis, entitled "EVALUATION OF ELECTRIC FIELD GRADIENTS IN MOLECULES USING SEMI-EMPIRICAL MO FORMALISMS" has been carried out by Mr. P.P. Thankachan under my supervision and that the same has not been submitted elsewhere for a degree.

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SYNOPSIS

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The present thesis is an attempt, to evaluate the performance of three different semi-empirical MO formalisms vis-a-vis the rigorous evaluation of electric field gradients (EFG) by ab initio quantum mechanical procedures and experiments. The formalisms selected for study are the CNDO/2 and INDO methods of Pople et al., and a method due to Nanda and Narasimhan at the INDO level which uses a basis of Orthogonalised Atomic Orbitals referred to as the NN-INDO method. This method achieves rotational invariance while differentiating the s and p orbitals, and the p orbitals among themselves. EFG's at the sites of the quadrupolar nuclei D, Li, B, N and O in some selected molecules are studied. The EFG's are evaluated rigorously using calculated MO wave functions in these formalisms for the molecules under study, and the results are analysed in the light of other existing calculations and experiments to obtain an insight into the physico-chemical phenomena involved.

The thesis consists of five chapters and two appendices. References to the literature appear at the end of each chapter.

Chapter I forms an introduction to the work described in the thesis. The nature of the quadrupolar interaction is outlined and *ab initio* as well as empirical and semi-empirical methods of evaluating EFG's are critically evaluated.

Chapter II outlines the semi-empirical formalisms chosen, and describes the gaussian transform method used for calculating the integrals required for evaluating the EFG's.

Chapter III contains a study of the EFG's at the sites of quadrupolar nuclei in the linear molecules lithium hydride, hydrogen fluoride, carbon monoxide, nitrogen, hydrogen cyanide, cyanogen and acetylene. It is found that the deuterium field gradients obtained by the NN-INDO method are consistently higher than that obtained by the other two methods, and this is accounted for on the basis of the Burns exponents that are used in the NN-INDO method.

Chapter IV deals with the calculation of EFG parameters in some non-linear molecules. The molecules chosen for study are methane, ammonia, water, hydrazine and formaldehyde and the cyclic molecules pyrrole and furan. Both the field gradient and the asymmetry parameter are evaluated at the sites of the quadrupolar nuclei.

Chapter V contains our results using the three different semi-empirical formalisms for the various quadrupolar nuclear

sites in the molecules ethylene, methyl cyanide, methylamine, formamide, hydrogen peroxide, nitrous acid, diborane, borazine, boron trifluoride, nitrogen difluoride, fluorine monoxide and fluorine dioxide. Some interesting qualitative correlations involving chemical concepts like hybridisation, electronegativity, etc. are observed and reported along with the results for the field gradient parameter.

The thesis concludes with a few critical remarks on the use of semi-empirical methods for evaluation of EFG's.

Appendix I of the thesis gives a listing of a computer program used in this work for the evaluation of the diagonal component of the EFG. Appendix II lists the conversion factors used for the conversion of experimental nuclear quadrupole coupling data into EFG's.

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CHAPTER I

INTRODUCTION

I.1 The Nature of the Quadrupolar Interaction

A wide class of interesting phenomena have their origins in the interaction of the nuclear charge distribution with the surrounding electron distribution. Among these may be listed the hyperfine structure and isotope shifts in high resolution spectroscopy, quadrupole hyperfine structure in rotational spectra of molecules, quadrupole splitting in Mo'ssbauer lines, and the phenomenon of Nuclear Quadrupole Resonance (NQR).

Consider a nuclear charge distribution given as $\rho(\vec{r})$. The electron distribution surrounding the nucleus generates an electric potential $V(r)$. The interaction energy is given by

$$E = \int \rho(\vec{r}) V(\vec{r}) d\vec{r} \quad (I.1)$$

Expanding the potential $V(\vec{r})$ in a Taylor series about the origin, we get

$$\begin{aligned} E = & V(0) \int \rho(\vec{r}) d\vec{r} + \sum_i \left(\frac{\partial V}{\partial x_i} \right) x_i \int \rho(\vec{r}) d\vec{r} \\ & + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right) x_i x_j \int \rho(\vec{r}) d\vec{r} + \\ & \text{higher order terms} \end{aligned} \quad (I.2)$$

The first term gives the Coulomb 'monopole' energy which is independent of nuclear orientation. The second term, namely the electric dipole moment contribution, vanishes due to nuclear parity¹. In fact, it can be shown that, all nuclear electric moments of odd parity vanish. Hence, to fourth order, the interaction energy consists of the monopole and the quadrupolar terms.

This quadrupole term may be written as

$$E_Q = \frac{1}{2} \sum_{i,j} V_{ij} \int (x_i x_j - \frac{1}{3} r^2 \delta_{ij}) \rho(\vec{r}) d\vec{r} + \frac{1}{6} \sum_{i,j} V_{ij} \delta_{ij} \int \vec{r}^2 \rho(\vec{r}) d\vec{r} \quad (I.3)$$

The last term is rotationally invariant and hence is not of interest to us here. Defining

$$Q_{ij} = \int (3x_i x_j - r^2 \delta_{ij}) \rho(\vec{r}) d\vec{r} \quad (I.4)$$

We get

$$\begin{aligned} E_Q &= \frac{1}{6} \sum_{i,j} Q_{ij} V_{ij} \\ &= -\frac{1}{6} \bar{Q} \nabla \bar{E} \end{aligned} \quad (I.5)$$

This expresses the quadrupolar interaction energy as the product of two dyadics, the nuclear quadrupole moment

$$\bar{Q} = \int (3 \vec{r} \vec{r} - r^2 \bar{1}) \rho(\vec{r}) d\vec{r}$$

and the gradient of the electric field due to the external electron charge distribution having components

$$(\nabla E)_{ij} = -V_{ij} = -\left(\frac{\partial^2 V}{\partial x_i \partial x_j} \right)_o \quad (I.6)$$

where the subscript o on $\frac{\partial^2 V}{\partial x_i \partial x_j}$ denotes that this quantity is evaluated at the nuclear centre.

Since the field \bar{E} is produced by charges external to the nucleus, the field gradient tensor $\bar{\nabla} \bar{E}$ is traceless, i.e., V satisfies the Laplace's equation $\nabla^2 V = 0$, further, since

$\frac{\partial^2 V}{\partial x_i \partial x_j} = \frac{\partial^2 V}{\partial x_j \partial x_i}$, it is symmetric. Hence the electric field gradient (EFG) tensor has five independent components. Also, we can choose the coordinate system such that the off-diagonal elements vanish. Such a coordinate system is referred to as the principal axis system for the EFG tensor. When the field gradient has cubic symmetry, $V_{xx} = V_{yy} = V_{zz}$. Now, by Laplace's equation $V_{xx} + V_{yy} + V_{zz} = 0$; hence, $V_{xx} = V_{yy} = V_{zz} = 0$. In other words, the quadrupolar interaction vanishes.

The nuclear quadrupole moment tensor \bar{Q} is also traceless and symmetric, as can be seen from eqn. (I.4). It can be shown that the \bar{Q} tensor has effective cylindrical symmetry and hence $Q_{xx} = Q_{yy}$, and $Q_{ij} = 0$, if $i \neq j$. Since $\sum_i Q_{ii} = 0$, we have $Q_{xx} = Q_{yy} = -\frac{1}{2} Q_{zz}$. Thus, a single parameter is sufficient to specify the nuclear quadrupole moment, and, semiclassically we can write the interaction energy as

$$E_Q = \frac{1}{6} Q_{zz} (V_{zz} - \frac{1}{2} (V_{xx} + V_{yy})) \quad (I.7)$$

To obtain the quantum mechanical Hamiltonian from the classical energy given by (I.5) one uses the quantum mechanical operator for Q_{ij} . This gives the Quadrupolar Hamiltonian as

$$H_Q = \frac{1}{6} \sum_{i,j} V_{ij} Q_{ij}^{(op)} \quad (I.8)$$

To obtain the quadrupolar interaction energy, we need to evaluate the matrix elements of H_Q between the nuclear states $|I, m_I\rangle$, where I is the spin angular momentum quantum number of the

nucleus, and m_I is the z-component of the spin which has $(2I+1)$ values. Since the energy difference between the ground, and excited states of nuclei is far greater than E_Q , only the ground state of the nucleus need be considered. Hence, we need to evaluate only such matrix elements as

$$\langle I, m_I | Q_{ij}^{op} | I, m_I' \rangle$$

Since by the Wigner-Eckart theorem² the matrix elements of all traceless and symmetric second rank tensors are proportional, we may express the matrix element above in terms of the matrix element of another operator with the same symmetry as Q_{ij} ; in particular we can write

$$\langle I, m_I | Q_{ij}^{op} | I, m_I' \rangle = C \langle I, m_I | \frac{3}{2}(I_i I_j + I_j I_i) - \delta_{ij} I^2 | I, m_I' \rangle \quad (I.9)$$

where C is a constant independent of m_I , m_I' , i and j . To evaluate C we evaluate the matrix element in eqn. (I.9) for $m_I = m_I' = I$ and $i = j = z$.

Defining the scalar quantity Q such that

$$eQ = \langle I, I | Q_{zz}^{op} | I, I \rangle \quad (I.10)$$

now gives from eqn. (I.9)

$$\begin{aligned} eQ &= C \langle I, I | 3I_z^2 - I^2 | I, I \rangle \\ &= CI(2I - 1) \end{aligned} \quad (I.11)$$

For I values less than 1, eQ vanishes. Hence only nuclei with $I \geq 1$ need be considered here. From eqn. (I.11) we obtain,

$$C = eQ / I(2I - 1) \quad (I.12)$$

The quadrupolar Hamiltonian may be now written as

$$\mathcal{H}_Q = \frac{eQ}{6I(2I-1)} \sum_{i,j} V_{ij} \left(\frac{3}{2} (I_i I_j + I_j I_i) - \delta_{ij} I^2 \right) \quad (I.13)$$

Since, the energy is independent of the coordinate system, we can now transform to the principal axis system of the EFG tensor. Since, in this system $V_{ij} = 0$, if $i \neq j$, and as $\sum_i V_{ii} = 0$, we get

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} [V_{zz}(3I_z^2 - I^2) + (V_{xx} - V_{yy})(I_x^2 - I_y^2)] \quad (I.14)$$

Introducing the quantities

$$eq \equiv V_{zz} \quad (I.15)$$

$$\text{and } \eta = \left| \frac{V_{xx} - V_{yy}}{V_{zz}} \right| \quad (I.16)$$

where by convention the axes are chosen such that

$$|V_{zz}| > |V_{yy}| > |V_{xx}|$$

gives us the quadrupolar Hamiltonian as

$$\mathcal{H}_Q = \{e^2 q Q / 4I(2I-1)\} [(3I_z^2 - I^2) + \eta(I_x^2 - I_y^2)] \quad (I.17)$$

By definition, eq is the component of the EFG tensor having the largest magnitude, and η is the 'asymmetry parameter' having

numerical values between 0 and 1. η represents the departure of the EFG tensor from axial symmetry. These two quantities, viz., e^2qQ and η , together with the three Euler angles needed to specify the orientation of the principal axes, describe the EFG tensor completely.

The quantity e^2qQ is known as the 'Quadrupole Coupling Constant' (QCC). QCC and η are experimentally measurable by various techniques. From the chemists' point of view these quantities are of interest, since they reflect the nature of the electron distribution around the nuclei.

I.2 Experimental Determination of Quadrupole Coupling Constants and η 's

Several experimental methods are available for the determination of Nuclear Quadrupole Coupling Constants (NQCC's) and η 's. For studies in gas phase, the techniques of microwave spectroscopy, molecular beam magnetic resonance and molecular beam electric resonance methods are commonly used. For studies in liquid phase, Nuclear Magnetic Resonance (NMR) relaxation data are of some utility. For studies in solid state, NMR, Electron Spin Resonance (ESR), Nuclear Quadrupole Resonance (NQR) and Mössbauer effect techniques are commonly employed. Amongst these, the NQR technique has been the most widely used, since the main interaction probed is the quadrupolar interaction. Lucken³ has given an exhaustive review of the various experimental methods of determination of NQCC's and η 's.

The NQCC's and η 's are very sensitive to the state of aggregation of the molecules studied. Since most of the molecular quantum chemical calculations are done on isolated molecules, it is preferable to compare the theoretically predicted QCC's with gas phase measurements. From pure NQR studies in solids, it has been clearly established that the quadrupole interaction energies can vary considerably depending on intermolecular interactions⁴. The measured QCC's are fairly accurate, since the techniques of radio frequency spectroscopy are generally employed. In the past decade, tremendous strides⁵ have been made in the precise determination of QCC's and η 's of several nuclei, in a variety of molecules. The quantitative interpretation of these data is a matter of great interest to the theoretical chemist. In the next section, we shall highlight the theoretical aspects of the calculation of EFG's in molecules.

I.3 Ab Initio Evaluation of Electric Field Gradients in Molecules

The EFG tensor is determined by the electronic and nuclear contributions. The classical expressions for the EFG tensor components may be obtained treating the nuclei (other than the one at which the EFG is to be evaluated and which will be denoted by subscript A) and the electrons as point charges. The potential at the nucleus A is given by

$$V = \sum_p \frac{Z_p e}{r_{Ap}} \quad (I.18)$$

where Z is the charge on the particle p and r_{Ap} is the distance between the nucleus A and the particle p . The components of the EFG tensor may be obtained readily from (I.18) as

$$V_{ij} = \frac{\partial^2 V}{\partial x_i \partial x_j} = \sum_p Z_p e \left\{ \left[\frac{3x_{ip} x_{jp} - \delta_{ij} r_p^2}{r_{Ap}^5} \right] \right\} \quad (I.19)$$

Quantum mechanically the quantities V_{ij} are then given by the expectation value of $V_{ij}^{(op)}$ as given by (I.19). Within the Born-Oppenheimer approximation we can treat the nuclei as stationary and write

$$V_{ij} = e \sum_{B \neq A} Z_B \frac{3x_{iAB} x_{jAB} - \delta_{ij} r_{AB}^2}{r_{AB}^5} - \left\langle \psi \left| \sum_S \left(\frac{3x_{iAS} x_{jAS} - \delta_{ij} r_{AS}^2}{r_{AS}^5} \right) \right| \psi \right\rangle \quad (I.20)$$

Here B runs over all the nuclei other than A and S runs over all the electrons in the system. In particular, for V_{zz} we have

$$\begin{aligned} eq_{zz} &= e \sum_{B \neq A} Z_B \left(\frac{3 \cos^2 \theta_{AB} - 1}{r_{AB}^3} \right) - \\ &\quad e \left\langle \psi \left| \sum_S \left(\frac{3 \cos^2 \theta_{AS} - 1}{r_{AS}^3} \right) \right| \psi \right\rangle \\ &= \langle eq_{zz} \rangle_{\text{nucl.}} + \langle eq_{zz} \rangle_{\text{elec.}} \end{aligned} \quad (I.21)$$

ψ in these equations is the total electronic wave function for the system. Several choices are available for the molecular wave function ψ in eqn. (I.21). For instance, we may have a

valence-bond or a molecular orbital or a correlated etc. type of wave function. If the molecular wave function is adequately described by a single Slater determinant of molecular orbitals (MO), i.e., considering the closed-shell case, we have

$$\psi = \frac{1}{\sqrt{(2n)!}} |\phi_1 \alpha(1) \phi_1 \beta(2) \dots \phi_n \beta(2n)| \quad (\text{I.22})$$

where the ϕ 's are individual MO's and $2n$ is the total number of electrons. Each of the ϕ 's may be expanded in terms of a set of atomic orbitals (AO) χ_k

$$\phi_i = \sum_k c_{ik} \chi_k \quad (\text{I.23})$$

This is the well-known LCAO MO approximation. With this approximation eqn. (I.21) reduces to

$$\begin{aligned} \langle \text{eq}_{zz} \rangle_A &= \langle \text{eq}_{zz} \rangle_{\text{nuc1.}} + \sum_i \langle \phi_i | \text{eq}_{zz} | \phi_i \rangle \\ &= e \sum_{B \neq A} Z_B \left(\frac{3 \cos^2 \theta_{AB} - 1}{r_{AB}^3} \right) - \sum_i^{\text{occ}} \sum_k \sum_l 2c_{ik} c_{il} (q_{kl})_A \end{aligned} \quad (\text{I.24})$$

where

$$(q_{kl})_A = \int \chi_k \chi_l \left(\frac{3 \cos^2 \theta_A - 1}{r_A^3} \right) d\tau \quad (\text{I.25})$$

Here the index i runs over all occupied MO's and k and l run over AO's.

Defining \bar{P} , the charge-and bond-order matrix, as

$$(\bar{P})_{kl} = \sum_{i=1}^{\text{occ}} 2 c_{ik} c_{il} \quad (\text{I.26})$$

and considering the quantities q_{kl} as forming a matrix \bar{q} , eqn. (I.25) may also be written as

$$\langle eq_{zz} \rangle_A = e \sum_{B \neq A} z_B \left(\frac{3 \cos^2 \theta_{AB} - 1}{r_{AB}^3} \right) - e \text{Tr}(\bar{P} \bar{q}_A) \quad (\text{I.27})$$

Similar expressions are obtained for the other EFG components as well.

An exact calculation of the EFG components for a molecular system in the ICAO-MO framework requires the evaluation of integrals of the type

$$\int \chi_k \chi_l q_A^{\text{op}} d\tau = \int \chi_k \chi_l \left(\frac{3x_{iA} x_{jA} - \delta_{ij} r_A^2}{r_A^5} \right) d\tau \quad (\text{I.28})$$

Since q_A^{op} is a one-electron operator these integrals may be of one-, two-, or three-centre variety depending on the particular AO's involved in each case. The task of evaluating these integrals increases in going from one- to two- to three-centre type. While the evaluation of one-centre type integrals with Slater type orbitals (STO) is fairly straight forward, the evaluation of two- and three-centre integrals is rather difficult. Due to the r^{-3} operator form, closed expressions for two- and three-centre integrals over STO's are not generally available in the literature. In fact, complete evaluation of all integrals was not routinely feasible till the work of Kern and Karplus⁷ appeared. Prior to this, studies were made mainly on diatomic molecules, where only one- and two-centre integrals need be evaluated.

With reference to ab initio calculations⁸, one of the most important factors to be considered is the nature of the basis set used. The most common basis set for molecular calculations are the nodeless STO's. These, however, are not altogether satisfactory in simulating the Hartree-Fock AO's when used singly. Therefore, extended basis sets are used. From the point of view of computational simplicity the gaussian wave functions⁹ are to be preferred. Many authors have therefore expanded STO's in terms of gaussians and proceeded with the evaluation of the integrals. The gaussian functions suffer from the fact that they have poor cusp behaviour. In order to improve upon the quality of the Hartree-Fock molecular wave functions, configuration interaction (CI) methods have been employed. It must, however, be pointed out here that the number of integrals to be evaluated becomes very large with such wave functions and computations are therefore generally limited to small molecules. With particular reference to EFG calculations using ab initio methods we may refer the reader to an excellent recent review by Moccia and Zandomenighi¹⁰. The theoretically calculated EFG values in molecules are very sensitive to changes in the geometry. Detailed studies have shown that, the 'frozen nucleus' calculations have to be supplemented by vibrational averaging over the nuclear motion, in order to obtain good agreement with experimental results. Such calculations typify the sophistication to which the ab initio methods have been developed for the

calculation of EFG's. With the availability of such precise calculations of EFG's one can even obtain the value of the nuclear quadrupole moment from the experimental QCC's. This is particularly true of the quadrupole moment of deuterium, since very accurate hydrogen molecule wave functions are available.

I.4 Empirical and Semi-Empirical Estimates of EFG's in Molecules

Since, calculations of the EFG parameters by ab initio methods were not feasible in the earlier years, historically, empirical and semi-empirical determination of the EFG parameters in terms of qualitative valence concepts came first. The pioneering work in this direction was that of Townes and Dailey¹¹.

Referring to eqn. (I.25) the electronic contribution to the EFG at the nucleus of interest, A may be written as

$$\begin{aligned}
 \langle q_{zz} \rangle_{\text{elec.}, A} = & -2 \sum_i^{\text{occ}} \sum_k^{\text{on } A} c_{ik}^2 (q_{kk})_A + \\
 & 4 \sum_i^{\text{on } A} \sum_k^{\text{on } B \neq A} \sum_l^{\text{on } B \neq A} c_{ik} c_{il} (q_{kl})_A + \\
 & 2 \sum_i^{\text{on } A} \sum_l^{\text{on } B \neq A} c_{il}^2 (q_{ll})_A + 2 \sum_i^{\text{on } A} \sum_l^{\text{on } B \neq A} \sum_m^{\text{on } C \neq A} c_{il} c_{im} (q_{lm})_A \quad (\text{I.29})
 \end{aligned}$$

i refers to the occupied MO's. The index k refers to orbitals on atom A while l, m refer to orbitals centred on other atoms. This makes explicit the 'centeredness' of the various integrals involved.

The Townes-Dailey approximation may be now summarised as follows :

1. The terms $\sum_i \sum_{l \neq i} c_{il}^2 (q_{il})_A$ are assumed to cancel with the nuclear contributions from atom B.
2. The quantities $(q_{kl})_A$ are neglected in the simpler versions of the theory. This amounts to neglect of contributions of overlap densities involving, one orbital on the quadrupolar nucleus with the other on another atom. However, these contributions were estimated by Townes and Dailey to account for only ~ 5 percent of the total EFG.
3. The three-centre integrals $(q_{lm})_A$ are neglected.

As a consequence of these assumptions, we are now left with only the first term on the r.h.s. of eqn. (I.29). In the one-centre $(q_{kk})_A$ terms, we have integrals such as $\int \chi_k q_A \chi_{k'} d\tau$ where k and k' are orbitals centred on A. By symmetry, integrals involving s and s orbitals or s and p orbitals as χ_k and $\chi_{k'}$ respectively, vanish. With χ_k and $\chi_{k'}$ both as p orbitals or both as d orbitals or with either χ_k as s and $\chi_{k'}$ as d orbital, this integral does not vanish. The p-p terms are the most important ones, and in an sp basis set, when the d orbitals are absent, they are the only ones to be accounted for.

Using the well-known forms for the hybrid orbitals, expressions^{3,12-14} for $(q_{zz})_A$ based on the Townes-Dailey approach are available. The EFG's are expressed in terms of electron

populations on the p orbitals of the atom in question. All these expressions also involve the field gradient due to the p-orbital of the free atom, which is used as a parameter. Further, conceptual parameters such as hybridisation, ionic character and pi character enter the expansions, making the prediction of EFG's by this approach less objective and too empirical. The contributions from the inner core of atoms are completely neglected. Thus the Sternheimer effects¹⁵ are ignored. Some attempts have been made to remedy some of the drawbacks in the Townes-Dailey approach. Particular mention may be made here of the work of Cotton and Harris¹⁶, Sichel and Whitehead¹⁷ and White and Drago¹⁸. Although these authors have attempted to decrease some of the deficiencies of the Townes-Dailey approach, they still either neglect some of the terms in eqn. (I.29) completely or approximate them with some rough estimates, and in this process heavily parametrise the calculations. It has been shown by O'Konski and Ha¹⁹ that the approximation used by Cotton and Harris for the two centre integrals, is rather unsatisfactory. Many authors^{3,13,14,17,21} have employed p-orbital populations obtained from semi-empirical as well as ab initio MO calculations with a view to correlate the EFG's of first and second row atoms, especially using the Townes-Dailey type approach and have obtained varying success. However, the parameter $(e^2qQ)_{\text{free atom}}$ employed in these calculations for a given atom has varied widely (-7 MHz to -14.1 MHz for ¹⁴N) and naturally, casts serious doubts on the

soundness of the procedure. In fact, very recently, Barber et al.²⁰ failed to obtain a correlation between their ab initio populations and ^{14}N EFG's in nitrogen containing compounds. In a recent work based on a version of semi-empirical MO formalism, referred to as MINDO/3, Dewar and coworkers²² have calculated EFG's at N-site in some molecules. These authors have employed the point-charge approximation for the two-centre integrals and the Mulliken type approximation for the three-centre integrals. To our knowledge, at the semi-empirical SCF MO level, only two groups of workers^{23,24} have made a complete calculation of the EFG's based on eqn. (I.29) without approximating any of the integrals. However, both these calculations concern themselves with EFG's at the deuterium site only.

I.5 Scope of the Present Work

Amongst the semi-empirical MO formalisms²⁵, CNDO/2 and INDO formalisms have been extensively employed for the study of various molecular properties. However, as far as EFG's are concerned, the wave functions from these formalisms have been employed mostly in the framework of the Townes-Dailey approach. Claims regarding the superiority of these wave functions for EFG calculations cannot therefore be accepted without reservation. It is essential that these wave functions are properly tested for several nuclei and a variety of molecules, by the evaluation of EFG's with the inclusion of all the integrals in eqn. (I.29). Such a test has not been carried out so far. Two recent

calculations^{23,24} have addressed themselves to this point using only one nucleus, namely deuterium. In the present work, we have calculated the EFG's at D,B,N and O sites in about twenty five molecules using CNDO/2 and INDO wave functions with Slater exponents and including all integrals. We have also examined another version of the INDO method due to Nanda and Narasimhan²⁶ which differentiates between orbitals with different m_l values such as p_x , p_y and p_z and yet retains rotational invariance. It is well known that these semi-empirical formalisms with the neglect of differential overlap correspond to calculation over orthogonal atomic orbital (OAO) basis sets²⁷. Hence, in order to calculate the EFG's we have assumed that these semi-empirical MO's are over a non-overlapping basis and transformed them to an overlapping basis. This process is often referred to as 'deorthogonalisation'. All our calculations have been performed with deorthogonalised basis sets. Our results have been compared with ab initio results and experimental results, wherever available, in order to bring out strengths and weaknesses of these three semi-empirical formalisms. The evaluation of EFG's in molecules requires knowledge of the ground state wave functions only. Since the EFG operator is a one-electron operator and samples the region of space close to the nucleus, the behaviour of the semi-empirical wave functions in this region can be also properly assessed. The role of orbital exponents in the STO's used can also be examined, by their

effect on the calculated EFG's. Thanks to the work of Snyder and Basch²⁸ we have a compilation of ab initio results, on EFG's for several molecules, obtained using double zeta STO's in the basis set. We are thus in a fortunate position to compare uniformly the performance of the three semi-empirical MO formalisms mentioned earlier, against ab initio methods in most cases.

In Chapter II of the thesis we present an outline of the semi-empirical formalisms employed and also describe in detail the procedure for the evaluation of the EFG integrals. Chapter III presents and analyses our results on EFG's at ^2H , ^7Li , ^{14}N and ^{17}O sites in some linear molecules, while Chapter IV presents and analyses EFG results in some non-linear as well as cyclic molecules. Chapter V presents further results involving D, B, N and O sites in several typical molecules. The thesis concludes with some remarks and suggestions for future work.

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CHAPTER II

ALL-VALENCE ELECTRON SEMI-EMPIRICAL MO FORMALISMS
AND CALCULATIONS OF ELECTRIC FIELD GRADIENTS

II.1 General

The present calculations have been performed using three different semi-empirical all-valence electron ICAO-MO formalisms, all of which fall into the category of what is popularly known as 'Neglect of Differential Overlap' (NDO) methods¹⁻³. The nomenclature derives from the fact that certain two-electron integrals in the Hartree-Fock-Roothaan equations⁴ are neglected; this was paraphrased in the original literature as 'differential overlap is neglected' in these integrals. However, it has been shown⁵ that what these approximations do, is to simulate a calculation using a basis set of orthogonalised atomic orbitals (OAO). The more popular of these methods have been Complete Neglect of Differential Overlap (CNDO) and Intermediate Neglect of Differential Overlap (INDO) schemes^{2b}. Several schemes of integral evaluation and approximations have been implemented at these levels⁶. For example, a modification of the INDO method known as the MINDO method has been developed by Dewar and coworkers. Several versions of MINDO are available, MINDO/3 being the latest⁷. Another method the MCZDO (many-centre zero differential overlap) has been developed by Brown and Raby^{1f}. The most sophisticated of the NDO methods is the NDDO method, originally developed by Pople and coworkers^{1a}, but computationally implemented much later. These methods take into account only the valence shell of electrons, it being assumed that the inner 'core' of electrons is unaffected by bond formation. This

assumption, it must be pointed out here, has serious implications in the calculation of nuclear quadrupole coupling constants (NQCC) from theoretical values of EFG evaluated using 'valence only' schemes. It has been shown by Sternheimer⁸, that the nuclear quadrupole moment can polarise the surrounding spherical charge distribution and lead to field gradient contribution from closed-shells around the nucleus in question. This effect known as 'Sternheimer Shielding/Antishielding Effect' can be accounted for in the all-electron calculations. However, in 'valence only' calculations it is generally assumed that the Sternheimer Effect is either negligible or is constant in a series of related molecular environments. We shall return to this question later in this thesis.

We have chosen for our studies the CNDO/2 and INDO methods of Pople and coworkers^{2b}, and a method at the INDO level using an explicitly orthogonalised atomic orbital basis developed by Nanda and Narasimhan⁹ (NN-INDO).

II.2 ICAO-MO-SCF Methods and Approximations

We restrict ourselves to the closed-shell case, where the total wave function is expressible as a single determinant of doubly occupied molecular orbitals, and define our basis as the valence basis. For such a molecular system, the Hartree-Fock-Roothaan equations⁴ are

$$\sum_i c_{mi} (F_{ij} - E_m S_{ij}) = 0, \quad \text{for } j = 1, \dots, N \quad (\text{II.1})$$

where N is the number of basis functions and c_{mi} are the ICAO MO coefficients. Here S_{ij} is the overlap integral, and F_{ij} is given by

$$F_{ij} = H_{ij} + \sum_k \sum_l P_{kl} [(ij/kl) - \frac{1}{2}(ik/jl)] \quad (\text{II.2})$$

where H_{ij} is the one-electron core-Hamiltonian matrix element, P_{kl} is the charge density matrix element given by

$$\text{occ.}$$

$$P_{kl} = 2 \sum_m c_{mk} c_{ml} \quad (\text{II.3})$$

and

$$(ij/kl) = \int \int \phi_i(1) \phi_j(1) \frac{1}{r_{12}} \phi_k(2) \phi_l(2) d\vec{r}_1 d\vec{r}_2 \quad (\text{II.4})$$

Normalisation requires that

$$\sum_i \sum_j c_{mi} c_{mj} S_{ij} = 1 \quad (\text{II.5})$$

The set of equations (II.1) are to be solved iteratively, since the F matrix elements are themselves functions of the c 's via eqns. (II.2) and (II.3). The MO's thus obtained are popularly known as SCF MO's. The major stumbling block in the solution of eqn. (II.1) is the number and variety of two-electron integrals to be evaluated. However, if the basis set is orthogonal many of these integrals become zero or very small and may be neglected. It is observed that these integrals which become very small are the ones involving an overlap charge distribution of the type $\phi_i(1) \phi_j(1)$ with $i \neq j$, so that 'neglect of differential overlap', viz., neglect of $\phi_i(1) \phi_j(1) d\tau_1$, leads to a drastic reduction in the number of integrals. At the CNDO level, all integrals

involving an overlap charge distribution are neglected; at the INDO level, one-centre exchange integrals (ij/ij) are retained in addition to those integrals retained in the CNDO level; and NDDO retains, in addition, all integrals not involving a 'diatomic' overlap charge distribution. Also, because of the simulation of the effect of an OAO basis, S_{ij} in eqn. (II.1) may be replaced by δ_{ij} , so that the set of equations to be solved becomes

$$\sum_i c_{mi} (F_{ij} - E_m \delta_{ij}) = 0 \quad (\text{II.6})$$

and the normalisation condition becomes

$$\sum_i c_{mi}^2 = 1 \quad (\text{II.7})$$

Different approximations and parametrisations are employed in different semi-empirical methods. Thus, each semi-empirical method is characterised by the way the core-Hamiltonian matrix elements H_{ij} and the remaining two-electron integrals are evaluated. The overriding concern in semi-empirical MO theories in the choice of the parameters is the so-called 'invariance' problem. The exact solution to the Hartree-Fock-Roothaan equations has the property that the calculated results remain unchanged⁴ when orthogonal coordinate transformations are made. However, when approximations to the Fock matrix are made and some integrals are neglected, this property need no longer be satisfied automatically. Pople and coworkers^{1,2b} address themselves to the problem of 'rotational invariance' and their prescription to solve this problem is to use values for two-centre coulomb integrals and

off-diagonal core-Hamiltonian elements dependent only on the atoms concerned and not on the individual orbitals^{2b}. Pople suggests that the results be invariant under hybridisation also. Jug¹⁰, however, is of the view that invariance requirements can be met by employing even less drastic conditions than demanded by CNDO. Cook et al.⁵ emphasise that invariance is to be demanded of calculated properties and not of the integrals entering the calculation. Cook¹¹ is also of the view that the widely used invariance 'principle' of approximate MO theories is physically unreasonable and formally unnecessary. However, approximations of coulomb integrals by integrals over spherically symmetric s-orbitals, in order to ensure invariance, as is done in CNDO and INDO, may be a drastic step in that, it neglects important spatial distinctions among the highly directional p- and d- orbitals. This is likely to be of serious consequence as far as tensor properties like EFG are concerned.

We shall now examine in detail the expressions for the matrix elements in the three semi-empirical formalisms chosen by us, and indicate the relevant approximations and parametrisations employed. The diagonal elements of the core-Hamiltonian, H_{ii} , may be written as

$$H_{ii} = (i | - \frac{1}{2} \nabla^2 - \frac{Z}{r_A} | i) + \sum_{B \neq A} (i | - \frac{Z_B}{r_B} | i) \quad (\text{II.8})$$

where A is the nucleus on which orbital i is centred. It is seen that the first term is essentially 'atomic' whereas the terms

($i | - v_B | i$) are of the nature of 'corrections' for the presence of other nuclei. It is, therefore, usual to set

$$H_{ii} = U_{ii} + \sum_{B \neq A} V_i^B \quad (\text{II.9})$$

CNDO/2 Parametrisation

In the CNDO/2 method¹², the approximations and parametrisations used are the following :

- i) All exchange integrals, and three- and four- centre integrals are neglected.
- ii) The coulomb integrals are reduced to one per atom pair, and hence denoted as γ_{AB} . They are evaluated using the s-type AO's on the respective centres. Thus, no differentiation is made between s,p,d, orbitals.
- iii) Off-diagonal elements of H are taken to be proportional to the overlap integrals, the proportionality constant being characteristic of the atom pair.

$$H_{ij} = (S_{ij}/2) (\beta_A + \beta_B) \quad (\text{II.10})$$

where A,B are atoms on which orbitals i,j respectively are centred. The β 's are chosen empirically to obtain agreement with ab initio results. It may be pointed out that it is here that OAO simulation enters the theory, the off-diagonal elements given by eqn. (II.10) are just of the same order of magnitude as H_{ij} 's over an OAO basis⁵.

iv) U_{ii} is evaluated as

$$U_{ii} = -\frac{1}{2}(I_i + A_i) - (Z_A - \frac{1}{2}) \gamma_{AA} \quad (\text{II.11})$$

where I_i , A_i stand for the ionisation potential and electron affinity of the orbital i respectively and are obtained from atomic data. Z_A is the core charge for atom A and γ_{AA} is the one-centre electron repulsion integral.

v) V_i^B is evaluated as

$$V_i^B = -Z_B \gamma_{AB} \quad (\text{II.12})$$

INDO Parametrisation

In the INDO procedure of Pople, Beveridge and Dobosh¹³, as pointed out earlier, the major difference from CNDO is that, one-centre exchange integrals are retained. These are evaluated using Slater-Condon F and G parameters¹⁴. F^2 and G^1 integrals are obtained from spectral data while F^0 value is obtained theoretically as in CNDO, using Slater s -type AO's. Also, because of the introduction of F^2 and G^1 terms the precise expressions for U_{ii} are somewhat different from CNDO.

NN-INDO Parametrisation

The method of Nanda and Narasimhan⁹ (NN-INDO) is at the INDO level, but makes explicit use of Löwdin-Orthogonalised¹⁵ orbital basis. The orbital exponents are chosen by Burns' rules¹⁶. Nanda and Narasimhan consider the transformations of

AO's under coordinate transformations and arrive at the rotational invariance criterion^{9,17} for the one-centre coulomb integral J as

$$J_{ii} = J_{ii'} + 2 K_{ii'} \quad (\text{II.13})$$

where i and i' are orbitals corresponding to the same l value and $K_{ii'}$ is the one-centre exchange integral. Thus, Nanda and Narasimhan are able to differentiate orbitals with different m_l values in repulsion integrals of their INDO method, and still achieve rotational invariance, whereas in Pople's INDO procedure such a situation does not obtain. Also, Burns' rule exponents¹⁶ employed in NN-INDO are different for s and p orbitals, unlike the equal s and p Slater exponents used in the CNDO and INDO methods.

One-centre integrals (U_{ii} and the one-centre two-electron integrals) are derived from atomic data^{18,19} in such a way that eqn. (II.13) is satisfied; there is no equalisation of all coulomb integrals as in the case of CNDO or INDO of Pople. The quantities U_{ii} thus obtained are partitioned into a potential energy and a kinetic energy component as

$$U_{ii} = T_{ii} + V_i^A \quad (\text{II.14})$$

by making use of T_{ii} 's obtained by a suitable scaling of theoretical kinetic energy integrals over atomic orbitals orthogonalised to the core AO's. The V_i^A 's thus obtained by difference are

used for obtaining the framework corrections to the core-Hamiltonian V_i^B (see eqn. II.9) using the relation

$$V_i^B = Z_B \left[\frac{V_i^A}{Z_A} \exp(-2 \zeta_i R_{AB}) - (1 - \exp(-2 \zeta_i R_{AB})) \gamma_{AB} \right] \quad (\text{II.15})$$

which is easily seen to have the correct asymptotic behaviour. In the above expression γ_{AB} is the average repulsion integral between orbitals on A and orbitals on B, calculated using Ohno's relation²⁰

$$\gamma_{AB} = \frac{1}{[R_{AB}^2 + (2/\gamma_A + \gamma_B)^2]^{\frac{1}{2}}} \quad \text{in a.u.} \quad (\text{II.16})$$

The atomic γ 's are obtained by the method of Yamaguchi and Fueno²¹ used in conjunction with O'Leary's atomic data¹⁸. The two-centre coulomb integrals are also obtained from the above relation as

$$(ii/jj) = \frac{1}{[R_{ij}^2 + (2/(ii/ii) + (jj/jj))^2]^{\frac{1}{2}}} \quad (\text{II.17})$$

The off-diagonal core-Hamiltonian elements are obtained from the relation

$$H_{ij} = \frac{1}{2}(H_{ii} + H_{jj})S_{ij} + \frac{1}{2}(T_{ii} + T_{jj})S_{ij}(1 - |S_{ij}|) \quad (\text{II.18})$$

with the term $S_{ij}(1 - |S_{ij}|)$ evaluated over a diatomic coordinate system and then rotated to the molecular system to maintain rotational invariance²². The Hamiltonian over OAO's is obtained by transforming the H-matrix as

$$\bar{H} = S^{-1/2} H S^{-1/2} \quad (\text{II.19})$$

where the bar over H signifies OAO basis. The two-electron integrals from atomic data are used uncorrected, since it is known that they are not as severely affected by the OAO transformations as are the core-Hamiltonian elements^{11b}. The atomic parameters used in the NN-INDO calculations for the first row elements are given in Table II.1. The parameters for lithium were not readily available to us and hence we obtained them by extrapolation using a cubic polynomial fit of the values for Be, B, C and N as a function of atomic number.

II.3 Methods of Evaluation of Electric Field Gradient Integrals

For the evaluation of the EFG tensor components using an LCAO MO wave function it is necessary to evaluate integrals of the type

$$\left(\phi_k \left| \frac{3r_{iA}r_{jA} - r_A^2 \delta_{ij}}{r_A^5} \right| \phi_l \right) \quad (\text{II.20})$$

where $r_{iA}, r_{jA} \in \{x_A, y_A, z_A\}$ are the components of the radius vector connecting nucleus A (at which the EFG is desired) to a given electron, and ϕ_k, ϕ_l are the AO's used in the calculation. This gives rise to the following four types of integrals :

$$\text{Type I : } (\phi_k^A | O_A | \phi_l^A) \quad (\text{II.21a})$$

with both orbitals on the same centre as the operator (one-centre integrals).

$$\text{Type II : } (\phi_k^A | O_A | \phi_l^B) \quad (\text{II.21b})$$

(two-centre integrals)

Table II.1

Atomic Parameters for the First-Row Elements Used in the NN-INDO Method *

Parameter	H	Li	Be	B	C	N	O	F
U_{ss}	-14.65	-6.24	-17.95	-33.71	-52.14	-71.86	-97.83	-130.96
U_{pp}	0.0	-4.28	-12.63	-25.21	-40.88	-58.50	-78.12	-108.03
$F^0(ss) = (ss ss)$	18.12	6.99	9.00	10.59	12.03	13.59	15.42	16.92
$(pp pp)$	0.0	6.06	6.97	8.86	11.08	12.98	14.52	16.71
$(ss pp)$	0.0	5.409	7.428	9.56	11.41	12.58	14.48	17.16
$(pp p'p')$	0.0	5.484	6.218	7.86	9.84	11.588	12.464	11.41
$(sp sp)$	0.0	0.518	1.276	1.80	2.30	2.986	3.94	4.63
$(pp' pp')$	0.0	0.288	0.376	0.50	0.62	0.696	1.028	0.90
$F_o(pp)$	0.0	5.690	6.470	8.19	10.25	12.050	13.150	15.51
ζ_s	1.2	0.600	0.900	1.35	1.575	1.875	2.200	2.50
ζ_p	0.0	0.250	0.750	1.00	1.400	1.650	1.975	2.30
T_{ss}	10.0	2.070	8.190	22.87	30.000	43.010	60.220	79.19
T_{pp}	0.0	0.200	2.900	5.10	10.000	13.890	19.900	27.00

All energy quantities in eV.

* See Reference 9.

$$\text{Type III : } (\phi_k^B | O_A | \phi_1^B) \quad (\text{II.21c})$$

(two-centre integrals)

$$\text{Type-IV : } (\phi_k^B | O_A | \phi_1^C) \quad (\text{II.21d})$$

(three-centre integrals).

Type I integrals are easy to evaluate in closed form over the STO basis set by separation of variables. Edlund et al.^{23a} have listed formulae for some of these. In the past, calculations of EFG using the NDO methods have mostly neglected the two- and three-centre integral contributions to the EFG operator. The importance of two- and three-centre integrals in the evaluation of EFG's by semi-empirical MO theories was recognised by Dewar and coworkers^{23b}. However, in their MINDO/3 studies they used only approximate values for these integrals. In the case of EFG calculations involving deuterium, there is no justification to discard the two- and three-centre contributions since the 1s contribution to EFG is zero by symmetry. Hence, to have a consistent scheme of evaluation of EFG using semi-empirical NDO methods, we need to incorporate the two- and three-centre integrals. To our knowledge there are only two studies^{24,25} reported in the literature where all the two- and three-centre EFG integrals have been evaluated in a semi-empirical MO calculation. However, these two studies have concerned themselves solely with deuterium.

The two- and three-centre integrals need careful handling, especially with regard to the diagonal components of the EFG

tensor. Because of the singularity of the integrand at the nucleus, the integrals are conditionally convergent for some functions and the value of the integral will depend upon the way the region around the singularity is handled²⁶. Stephen and Auffray²⁷ noted this in their work on HD^+ , and evaluated the integral by a numerical integration method with a spherical volume around the nucleus excluded; they thus obtained the limit as the excluded volume tends to zero. Subsequently it was shown^{28,29}, that the same effect is achieved by adding to the integrand a term equal to $4\pi/3$ times a delta function centred at the singular point. This has been noted also in the work of Kolker and Karplus³⁰ and Kern and Karplus³¹. McConnell and Strathdee³² failed to take account of this in their work on esr hyperfine coupling as was pointed out by Pitzer et al.²⁹

For Type II integrals methods based on prolate spheroidal coordinate systems or the Barnett-Coulson expansion³³ may be used. In the methods based on the prolate spheroidal coordinate systems, these integrals (as also others having r^{-n} in the integrand, with $n > 1$) necessitate new auxiliary functions in addition to the usual $A_n(a)$ and $B_n(b)$ functions³⁴. Kolker and Karplus³⁰ generalised Ormand's $\text{Eu}_n(x,y)$ functions³⁵ to define

$$E_n^m(a,b) = \int_1^\infty d\lambda \int_{-1}^1 d\mu \exp(-a\lambda - b\mu) \frac{\mu^n (1-\mu^2)^{m-1}}{(\lambda-\mu)^m} \quad (\text{II.22})$$

which along with the $A_n(a)$ and $B_n(b)$ functions lead to the

required integral formulae. Huo and Roothaan³⁶ developed a method based on auxiliary functions related to Roothaan's $C_{\alpha,\beta}^{\gamma,\delta,t}$, but the details are not available in the literature. Barfield and coworkers²⁵ have published formulae for integrals involving 1s orbital on centre A (vide eqn. II.21b) and 1s, 2s and 2p orbitals on centre B based on the expansion method of Barnett and Coulson.

Type III integrals were evaluated by McConnell and Strathdee³² who failed to take into account the δ -function and thus were led to wrong results, as was pointed out by Pitzer et al.²⁹. Pitzer et al. made use of expansions of the operator on centre A onto centre B following Hobson³⁷. Recently, Edlund et al.^{23a} evaluated these integrals but Barfield and coworkers²⁵ have pointed out some errors in their results, and have also listed explicit formulae involving orbitals upto 2p based on the earlier work of Barfield^{38,39}.

For Type IV (three-centre) integrals the only available method seems to be the 'Gaussian-Transform Method' of Shavitt and Karplus^{40,41}. For the EFG integrals this method was adopted by Kern and Karplus³¹. The Gaussian-transform (GT) method has the advantage that in the limit as the nuclear centres are made to approach each other, the formulae go over to the correct two-centre formulae. We have in the present work evaluated all the integrals other than one-centre integrals by the GT method. In spite of the fact, that specialised methods are computationally

cheaper for the two-centre integrals we have employed the GT method for these also because of its ease for computer programming. In the next section we give an account of the GT method.

II.4 The Gaussian Transform Method for Evaluation of EFG Integrals

Here use is made of the facts that many centre integrals involving gaussian functions are easy to evaluate, and that STO's can be expressed as integral transforms of gaussian functions^{40,41}. For example, the 1s-STO may be written as

$$e^{-\zeta r} = \frac{\zeta}{2\sqrt{\pi}} \int_0^{\infty} s^{-3/2} e^{-\zeta^2/4s} e^{-sr^2} ds \quad (\text{II.23})$$

The method essentially consists in obtaining the expression for the integral involving the 1s-type GTO's and then obtaining the 1s-STO formulae therefrom by applying the transform (eqn.II.23) to each GTO used. The basic 1s-STO formulae, then, become the starting point for derivation of the higher orbital formulae by the differential operator technique. We outline the method in three stages as indicated above, viz.,

- i) the derivation of 1s Gaussian formulae,
- ii) obtaining the 1s exponential formulae therefrom and
- iii) generation of higher orbital formulae.

The treatment given here for the diagonal components of EFG follows Kern and Karplus³¹ with some notational changes. The expressions for the off-diagonal components have been derived

by the author along the same lines. For convenience in formula generation we express the formulae in terms of the J_{lm} functions rather than the T_{lm} 's used by Kern and Karplus.

II.4.1 Gaussian 'ls' Formulae

For purposes of illustration, we shall consider in particular two of the EFG integrals, namely, those involving the q_{zz} and q_{xy} operators. The problem of singular integrands occurs with the diagonal components q_{xx} , q_{yy} and q_{zz} . It has been demonstrated that the physically correct value is obtained by adding a term equal to $4\pi/3$ times a delta function about the singular point for these integrals. Thus we may write for operators centred at C

$$q_{zz,C} = \frac{3z_C^2 - r_C^2}{r_C^5} = \frac{\partial^2}{\partial z_C^2} (1/r_C) + \frac{4\pi}{3} \delta(r_C) \quad (\text{II.24})$$

and

$$q_{xy,C} = \frac{3x_C y_C}{r_C^5} = \frac{\partial^2}{\partial y_C \partial x_C} (1/r_C) \quad (\text{II.25})$$

Let us consider the three-centre case, where 1s gaussian functions on centres A and B, assumed distinct from C, are involved. For $q_{zz,C}$ we get using eqn. (II.24) the relation

$$I_G = \int d\bar{r} \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \frac{\partial^2}{\partial z_C^2} (1/r_C) + 4\pi/3 \int d\bar{r} \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \delta(r_C) \quad (\text{II.26})$$

Because of the distinctness of the centres A, B and C, the operator $\partial^2/\partial z_C^2$ leaves the exponential part in the first term

unaffected, so that we can, after interchange of integration and differentiation operations, write

$$I_G = \frac{\partial^2}{\partial z_C^2} \int d\vec{r} \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) (1/r_C) + 4\pi/3 \int d\vec{r} \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \delta(r_C) \quad (\text{II.27})$$

Now the integral in the first term in the r.h.s. of eqn. (II.27) is the three-centre nuclear-attraction integral, which has been evaluated through the use of the auxiliary functions⁴⁰

$$F_m(t) = \int_0^1 u^{2m} \exp(-tu^2) du \quad (t > 0, m = 0, 1, \dots) \quad (\text{II.28})$$

which obey the recursion relations

$$F_{m+1}(t) = -\frac{d}{dt} F_m(t) \quad (\text{II.29})$$

and

$$F_m(t) = \frac{1}{2m+1} (2t F_{m+1}(t) + e^{-t}) \quad (\text{II.30})$$

The second term in the r.h.s. of eqn. (II.27) may also be evaluated using the same auxiliary functions. We define

$$a_x = x_A - x_B \text{ with similar relations for } a_y, a_z; \\ \overline{AB}^2 = a_x^2 + a_y^2 + a_z^2; \quad (\text{II.31})$$

$$P_x = (\alpha_1/\alpha_1+\alpha_2) x_A + (\alpha_2/\alpha_1+\alpha_2) x_B; \\ P_y = (\alpha_1/\alpha_1+\alpha_2) y_A + (\alpha_2/\alpha_1+\alpha_2) y_B; \text{ and} \\ P_z = (\alpha_1/\alpha_1+\alpha_2) z_A + (\alpha_2/\alpha_1+\alpha_2) z_B$$

and \overline{PC} as the length of the vector joining (P_x, P_y, P_z) to C. This leads to

$$I_G = (2\pi/(\alpha_1 + \alpha_2)) \frac{\partial^2}{\partial z_C^2} \{ F_0[(\alpha_1 + \alpha_2) \overline{PC}^2] \exp[-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2] \} +$$

$$4\pi \{ F_1[(\alpha_1 + \alpha_2) \overline{PC}^2] - (2/3)(\alpha_1 + \alpha_2) \overline{PC}^2 F_2[(\alpha_1 + \alpha_2) \overline{PC}^2] \} \times$$

$$\exp(-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2) \} \quad (\text{II.32})$$

Performing the indicated differentiations using eqn. (II.29) leads to

$$I_G = \frac{8\pi}{3} (\alpha_1 + \alpha_2) [3 \overline{PC}_z^2 - \overline{PC}^2] F_2[(\alpha_1 + \alpha_2) \overline{PC}^2] \times$$

$$\exp[-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2] \quad (\text{II.33})$$

Similarly for the q_{xy} operator we get

$$I_G' = \int \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \frac{\partial^2}{\partial x_C \partial y_C} (1/r_C) d\bar{r}$$

$$= \frac{\partial^2}{\partial x_C \partial y_C} \int \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) (1/r_C) d\bar{r}$$

$$= 8\pi(\alpha_1 + \alpha_2) \overline{PC}_x \overline{PC}_y F_2[(\alpha_1 + \alpha_2) \overline{PC}^2] \times \exp[-\frac{\alpha_1 \alpha_2}{\alpha_1 + \alpha_2} \overline{AB}^2] \quad (\text{II.34})$$

Now let us consider the two-centre case. Here let us assume that centres B and C coincide. We may write then

$$I_{G, B=C} = \int \exp(-\alpha_1 r_A^2 - \alpha_2 r_C^2) \frac{\partial^2}{\partial z_C^2} (1/r_C) d\bar{r}$$

$$= \int \{ \lim_{B \rightarrow C} \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \} \frac{\partial^2}{\partial z_C^2} (1/r_C) d\bar{r} \quad (\text{II.35})$$

Assuming that the limit and integration operations may be interchanged, we now get

$$I_{G,B=C} = \lim_{B \rightarrow C} \int \exp(-\alpha_1 r_A^2 - \alpha_2 r_B^2) \frac{\partial^2}{\partial z_C^2} (1/r_C) d\bar{r} \quad (\text{II.36})$$

so that the two-centre formulae may be obtained as limits of the general three-centre formulae.

II.4.2 Formulae Over 1s-STO's

As before, we consider the case of the q_{zz} operator. Using eqn. (II.23) we can write the product of two 1s-functions centred on A and B as

$$\begin{aligned} (1s)_A (1s)_B &= \exp(-\xi_1 r_A - \xi_2 r_B) \\ &= \frac{\xi_1 \xi_2}{4\pi} \int_0^\infty \int_0^\infty (\alpha_1 \alpha_2)^{-3/2} \times \exp\left[-\frac{1}{4}\left(\frac{\xi_1^2}{\alpha_1} + \frac{\xi_2^2}{\alpha_2}\right)\right] \times \\ &\quad \exp[-(\alpha_1 r_A^2 + \alpha_2 r_B^2)] d\alpha_1 d\alpha_2 \end{aligned} \quad (\text{II.37})$$

so that the required integral becomes

$$\begin{aligned} I_E &= \int \frac{3 z_C^2 - r_C^2}{r_C^5} (1s)_A (1s)_B d\bar{r} \\ &= \frac{\xi_1 \xi_2}{4\pi} \int_0^\infty d\alpha_1 \int_0^\infty d\alpha_2 (\alpha_1 \alpha_2)^{-3/2} \exp\left[-\frac{1}{4}\left(\frac{\xi_1^2}{\alpha_1} + \frac{\xi_2^2}{\alpha_2}\right)\right] \times \\ &\quad \left\{ \int d\bar{r} \frac{3 z_C^2 - r_C^2}{r_C^5} \exp[-\alpha_1 r_A^2 - \alpha_2 r_B^2] \right\} \end{aligned} \quad (\text{II.38})$$

where the factor within the braces is easily seen to be I_G in eqn. (II.26) and which has been already considered in detail in Section II.4.1.

Substituting for I_G from eqn. (II.33) and defining the following variables

$$t = \alpha_1 + \alpha_2 ; \quad u = \frac{\alpha_1}{\alpha_1 + \alpha_2} ;$$

$p_x = u x_A + (1-u) x_B - x_C$ and other similar equations for p_y, p_z ;

$$w = p^2 = p_x^2 + p_y^2 + p_z^2 ; \quad (II.39)$$

$$f = u(1-u) \overline{AB}^2 ; \quad \text{and}$$

$$g = \frac{1}{4} \left(\frac{\xi_1^2}{u} + \frac{\xi_2^2}{1-u} \right)$$

leads to the expression

$$I_E = \frac{2 \xi_1 \xi_2}{3} \int_0^1 du \int_0^\infty dt [u(1-u)]^{-3/2} t^{-1} \exp(-ft - g/t) \times \\ (3p_z^2 - p^2) F_2(wt) \quad (II.40)$$

We note that \overline{AB} in the above denotes the distance between points A and B.

Using the auxiliary function

$$J_{n,m}(w,f,g) = \int_0^\infty dt t^{n-1/2} F_m(wt) \exp(-ft - g/t) \quad (II.41)$$

the expression for I_E reduces to

$$I_E = \frac{2 \xi_1 \xi_2}{3} \int_0^1 du \frac{3p_z^2 - p^2}{[u(1-u)]^{3/2}} J_{\frac{1}{2},2} \quad (II.42)$$

Now the integral evaluation can be done provided the function $J_{\frac{1}{2},2}$ can be evaluated. This can be done using the known series expansion for $F_m(t)$ in eqn. (II.40). Another approach to the evaluation of the $J_{n,m}$ functions is via the related functions

$$\begin{aligned}
T_{1,m}(\sigma, \tau) &= J_{1-m,m}(1, \sigma, \tau) / \Gamma(m + \frac{1}{2}) \\
&= w^{m-1+\frac{1}{2}} J_{1-m,m}(w, f, g) / \Gamma(m + \frac{1}{2})
\end{aligned} \tag{II.43}$$

where

$$\sigma = f/w, \quad \tau = gw$$

We have

$$\begin{aligned}
T_{1,m}(\sigma, \tau) &= J_{1-m,m}(1, \sigma, \tau) / \Gamma(m + \frac{1}{2}) \\
&= \frac{1}{\Gamma(m + \frac{1}{2})} \int_0^{\infty} t^{m-1-\frac{1}{2}} F_m(t) \exp(-\sigma t - \frac{\tau}{t}) dt
\end{aligned} \tag{II.44}$$

Substituting for $F_m(t)$ from eqn. (II.28) and reversing the order of integrations leads to

$$T_{1,m}(\sigma, \tau) = \frac{2}{\Gamma(m + \frac{1}{2})(2\tau)^{1-m-\frac{1}{2}}} \int_0^1 v^{2m} k_{1-m-\frac{1}{2}} \{ 2[\tau(\sigma+v^2)] \} dv \tag{II.45}$$

where $k_n(x) = x^n K_n(x)$, $K_n(x)$ being the modified Bessel function of the second kind⁴². The integrand being a smooth function, $T_{1,m}(\sigma, \tau)$ may be evaluated by gaussian quadrature. In the present work the functions $K_n(x)$ are evaluated directly for $n = 0, 1$ and through the recursion formula⁴²

$$K_{n+1}(x) = K_{n-1}(x) + \frac{2n}{x} K_n(x) \tag{II.46}$$

for higher values of n . $K_0(x)$ and $K_1(x)$ are evaluated from their series expressions⁴² for $0 < x < 2$ and by a polynomial approximation⁴³ for $x > 2$. The reduced functions $k_n(x)$ are obtained from the $K_n(x)$ and used in the evaluation of the T_{1m} 's and thereby the $J_{1,m}$ functions needed.

As for the q_{xy} EFG operator, we have similarly

$$I_E' = 2 \zeta_1 \zeta_2 \int_0^1 \frac{p_x p_y}{[u(1-u)]^{3/2}} J_{\frac{1}{2},2}(w,f,g) \quad (II.47)$$

with the same notation as defined in eqn. (II.39).

II.4.3 Higher Exponential Orbitals

Relations such as

$$\begin{aligned} r_A e^{-\zeta_1 r_A} &= -\frac{\partial}{\partial \zeta_1} e^{-\zeta_1 r_A} \\ x_B e^{-\zeta_2 r_B} &= -\frac{\partial}{\partial \zeta_2} \frac{1}{\zeta_2} \frac{\partial}{\partial x_B} e^{-\zeta_2 r_B} \text{ etc.} \end{aligned} \quad (II.48)$$

are used in generating the formulae involving higher exponential orbitals. One simply differentiates the 1s - formula with respect to the parameters appropriate in each case. However, this tends to be a tedious and error-prone task if done manually. Hence, these formulae have been generated by us automatically using a computer program with the aid of the 'replacement operator technique'. To illustrate this technique^{40,41}, consider a general term in the formula

$$\begin{aligned} \theta = \zeta_1^{a_1} \zeta_2^{a_2} \int_0^1 u^{-3/2 + n_1} (1-u)^{-3/2 + n_2} p_x^{l_1} p_y^{l_2} p_z^{l_3} x \\ a_x^{m_1} a_y^{m_2} a_z^{m_3} J_{n,m}(w,f,g) du \end{aligned} \quad (II.49)$$

with the notations as defined in eqn. (II.39).

The effect of an operator such as $-\frac{\partial}{\partial \zeta_1}$ may be found using the chain rule, which generates a number of terms with modified values of the indices a_1, a_2, \dots , etc. That is, we may look

upon this operator as a sum of 'replacement operators' which modify some of the indices, and multiply the resulting terms with appropriate numerical coefficients. For example, we have

$$-\frac{\partial \theta}{\partial \zeta_1} = -a_1 R \left(\begin{smallmatrix} a_1-1 \\ a_1 \end{smallmatrix} \right) + \frac{1}{2} R \left(\begin{smallmatrix} a_1+1 & n_1-1 & n+1 \\ a_1 & n_1 & n \end{smallmatrix} \right) \quad (\text{II.50})$$

Here we have used the relations

$$\begin{aligned} \frac{\partial J_{n,m}(w,f,g)}{\partial w} &= -J_{n-1,m+1}(w,f,g) \\ \frac{\partial J_{n,m}(w,f,g)}{\partial f} &= -J_{n-1,m}(w,f,g) \quad , \quad \text{and} \\ \frac{\partial J_{n,m}(w,f,g)}{\partial g} &= -J_{n+1,m}(w,f,g) \end{aligned} \quad (\text{II.51})$$

which follow from the definitions of the $J_{n,m}$'s and eqn.(II.29).

A given higher orbital formula is obtained by successively applying appropriate replacement operators. This can be coded for a digital computer representing each term by a coefficient and a set of numerical values forming components of a vector; like terms are collected out of the resulting terms and the appropriate coefficient and indices printed out. The formulae so generated are coded for computation.

For the purpose of formula generation the q_{zz} formula is represented by a sum of two terms, as

$$(1s | q_{zz} | 1s) = T_1 + T_2$$

where

$$T_1 = 2 \, \zeta_1 \, \zeta_2 \int_0^1 \frac{p_z^2}{[u(1-u)]^{3/2}} J_{\frac{1}{2},2}(w,f,g) \, du$$

and

(II.52)

$$T_2 = -(2/3) \, \zeta_1 \, \zeta_2 \int_0^1 \frac{p_z^2}{[u(1-u)]^{3/2}} J_{\frac{1}{2},2}(w,f,g) \, du$$

In this case, the terms generated from both T_1 and T_2 are added to give the final result. For the q_{xy} EFG operator, the 1s - formulae consist of only one term and hence the formula generation is more straightforward. Formulae for all the components of the EFG operator have been similarly generated.

II.5 Testing of the Computer Program for Evaluation of Integrals

All the necessary integrals for the evaluation of EFG's have been obtained in the present work by means of computer programs written by the author himself in FORTRAN 10 and have been successfully executed in a DEC 1090 computer at the Indian Institute of Technology, Kanpur, India. Double precision has been used throughout.

Two versions of the programs were created, the first using 16-point gaussian quadrature both for evaluation of $J_{n,m}$ functions and for the final integration, and the second using 12-point gaussian quadrature instead. Since, Scrocco⁴⁴ has reported all the EFG integrals for the case of CO with orbital exponents from Slater's rules, we used the same for checking our results. The integral values from the 16-point are compared with his results in Table II.2. The agreement is perfect to the last digit

Table II.2

EFG Integrals for CO (16 Point Gaussian Quadrature)
(The values of Scrocco* are given in parentheses)

	$2s_0$	$2p_{x0}$	$2p_{y0}$	$2p_{z0}$	$2s_C$	$2p_{xC}$	$2p_{yC}$	$2p_{zC}$
$2s_0$	0.00000	0.00000	0.00000	0.00000	0.06197 (0.62000)	0.00000	0.00000	0.09729 (0.09730)
$2p_{x0}$	0.00000	-1.56994 (-1.57000)	0.00000	0.00000	0.00000	-0.04546 (-0.04544)	0.00000	0.00000
$2p_{y0}$	0.00000	0.00000	-1.56994 (-1.57000)	0.00000	0.00000	0.00000	-0.04546 (-0.04544)	0.00000
$2p_{z0}$	0.00000	0.00000	0.00000	3.13988 (-3.14000)	-0.22872 ** (0.22865)	0.00000	0.00000	-0.36041 ** (0.36035)
$2s_C$	0.06197	0.00000	0.00000	-0.22872 (0.12450)	0.12450 (0.12450)	0.00000	0.00000	0.10039 (0.10030)
$2p_{xC}$	0.00000	-0.04546	0.00000	0.00000	0.00000	0.08137 (0.08137)	0.00000	0.00000
$2p_{yC}$	0.00000	0.00000	-0.04546	0.00000	0.00000	0.00000	0.08137 (0.08137)	0.00000
$2p_{zC}$	0.09729	0.00000	0.00000	-0.36041	0.10039	0.00000	0.00000	0.21077 (0.21077)

* See Reference 44 of text.

** The sign difference in these two integrals is due to the difference in the choice of local coordinates.

reported by him, in all but the cases of $(2p_{\pi O} | q | 2p_{\pi C})$, $(2p_{\sigma O} | q | 2p_{\sigma C})$ and $(2p_{zO} | q | 2s_C)$ where there is agreement within 10^{-4} a.u. In Table II.3 we give the integral values obtained with the 12-point formulae. It can be seen that the values given in Tables II.2 and II.3 agree to within 10^{-4} a.u. We have therefore employed the 12-point version in our calculations since this results in a near-halving of computer time. Barfield et al.²⁵ have published values of the integrals for the components of the EFG tensor in the case of HCN with the exponents $\zeta_H = 1.24$, $\zeta_C = 1.72$, $\zeta_N = 1.95$ and distances $r_{CH} = 1.063 \text{ \AA}$, $r_{CN} = 1.5553 \text{ \AA}$. We calculated q_{zz} and q_{xy} for HCN using the same exponent and geometry as employed by Barfield et al. We used the 12-point version of our program. The results are compared in Tables II.4 and II.5. It can be seen from these tables that the agreement is excellent. We have also tested some two-centre integrals using the method of Pitzer et al.²⁹ and the method of Kolker and Karplus³⁰.

A listing of the EFG integral evaluation program written by the author is given in Appendix I. A table of conversion factors between EFG values in a.u. and nuclear quadrupole coupling constants (NQCC) values in frequency units for the nuclei 2D , 7Li , ^{11}B , ^{14}N and ^{17}O is given in Appendix II.

In the present work, we have calculated the EFG's for a variety of molecules using the semi-empirical MO formalisms, namely, CNDO/2, INDO and NN-INDO. Our results on molecules of

Table II.3
EFG Integrals for CO Using 12-Point Quadrature

	$2s_0$	$2p_{x0}$	$2p_{y0}$	$2p_{z0}$	$2s_C$	$2p_{xC}$	$2p_{yC}$	$2p_{zC}$
$2s_0$	0.00000	0.00000	0.00000	0.00000	0.06196	0.00000	0.00000	0.09728
$2p_{x0}$	0.00000	-1.56994	0.00000	0.00000	0.00000	-0.04549	0.00000	0.00000
$2p_{y0}$	0.00000	0.00000	-1.56994	0.00000	0.00000	0.00000	-0.04549	0.00000
$2p_{z0}$	0.00000	0.00000	0.00000	3.13988	-0.22882	0.00000	0.00000	-0.36049
$2s_C$	0.06196	0.00000	0.00000	-0.22882	0.12450	0.00000	0.00000	0.10039
$2p_{xC}$	0.00000	-0.04549	0.00000	0.00000	0.00000	0.08136	0.00000	0.00000
$2p_{yC}$	0.00000	0.00000	-0.04549	0.00000	0.00000	0.00000	0.08136	0.00000
$2p_{zC}$	0.09728	0.00000	0.00000	-0.36049	0.10039	0.00000	0.00000	0.21077

Table II.4

Integrals for q_{zz} in HCN
(Values given in parentheses are from
Barfield et al*)

	$1s_H$	$2s_C$	$2p_{xC}$	$2p_{yC}$	$2p_{zC}$	$2s_N$	$2p_{xN}$	$2p_{yN}$	$2p_{zN}$
$1s_H$	0.00000	0.07584 (0.0758)	0.00000	0.00000	0.11097 (0.1110)	0.00715 (0.0071)	0.00000	0.00000	0.01136
$2s_C$	0.07584	0.14812 (0.1481)	0.00000	0.00000	0.11935 (0.1193)	0.02717 (0.0272)	0.00000	0.00000	0.03706 (0.0371)
$2p_{xC}$	0.00000	0.00000	0.09677 (0.0968)	0.00000	0.00000	0.00000	0.01230 (0.0123)	0.00000	0.00000
$2p_{yC}$	0.00000	0.00000	0.00000	0.09677 (0.0968)	0.00000	0.00000	0.00000	0.01230 (0.0123)	0.00000
$2p_{zC}$	0.11097	0.11935	0.00000	0.00000	0.25082 (0.2508)	-0.01175 (-0.0118)	0.00000	0.00000	-0.00813 (-0.0081)
$2s_N$	0.00715	0.02717	0.00000	0.00000	-0.01175 (-0.0118)	0.02710 (0.0271)	0.00000	0.00000	0.01430 (0.0143)
$2p_{xN}$	0.00000	0.00000	0.01230	0.00000	0.00000	0.00000	0.02350 (0.0235)	0.00000	0.00000
$2p_{yN}$	0.00000	0.00000	0.00000	0.01230	0.00000	0.00000	0.00000	0.02350 (0.0235)	0.00000
$2p_{zN}$	0.01136	0.03706	0.00000	0.00000	-0.00813	0.01430	0.00000	0.00000	0.03433 (0.0343)

* See Reference 25.

Table II.5
Integrals for q_{xy} in HCN
(Values given in parentheses are from
Barfield et al.*)

	$1s_H$	$2s_C$	$2p_{xC}$	$2f_{yC}$	$2f_{zC}$	$2s_N$	$2p_{xN}$	$2p_{yN}$	$2p_{zN}$
$1s_H$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$2s_C$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$2p_{xC}$	0.00000	0.00000	0.00000	0.03299 (0.0330)	0.00000	0.00000	0.00000	0.00178 (0.0018)	0.00000
$2p_{yC}$	0.00000	0.00000	0.03299	0.00000	0.00000	0.00000	0.00178	0.00000	0.00000
$2p_{zC}$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$2s_N$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$2p_{xN}$	0.00000	0.00000	0.00000	0.00178	0.00000	0.00000	0.00000	0.00091 (0.0009)	0.00000
$2p_{yN}$	0.00000	0.00000	0.00178	0.00000	0.00000	0.00000	0.00091	0.00000	0.00000
$2p_{zN}$	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

* See Reference 25.

interest containing the quadrupolar nuclei ^2D , ^7Li , ^{11}B , ^{14}N , and ^{17}O are reported and discussed in the next three chapters of this thesis. Our calculated EFG values are quoted upto five decimal places and the asymmetry parameter values upto three decimal places uniformly in this thesis.

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CHAPTER III

ELECTRIC FIELD GRADIENTS IN SOME LINEAR MOLECULES

III.1 General

In the case of linear molecules the calculations of EFG's becomes a much simpler proposition than in the non-linear case, since now the molecular symmetry axis and the principal axis of the EFG tensor coincide. Therefore with the z-axis chosen along the molecular axis, the EFG tensor is diagonal, and by symmetry and the Laplace equation we have $q_{xx} = q_{yy} = -\frac{1}{2} q_{zz}$, i.e., the asymmetry parameter $\eta = 0$ and q_{zz} determines the EFG tensor completely. In order to test the three semi-empirical MO formalisms, in terms of their ability to predict the EFG's at various quadrupolar nuclear sites in linear molecules, we have chosen the following seven molecules viz. LiD, DF, DCN, DCCD, N₂, NCCN, and CO. The calculated EFG's for ²H, ⁷Li, ¹⁴N, ¹⁷O in these molecules have been compared with other theoretical and available experimental results. The experimental results are generally reported in the literature as quadrupole coupling constants in frequency units and these have been converted into EFG's in atomic units by us, using the conversion factors given in Appendix II. Our calculations have all been performed using the experimental bond distances for the molecules under study. The values of bond lengths used were taken from literature, and wherever possible from microwave determinations. The bond

distance data used in our calculations are presented in Table III.1.

Since our calculations make use of a valence basis set only for the electronic part, it is necessary that the nuclear contribution be calculated using a screened nuclear charge in place of the atomic number of the nucleus in question. For atoms from Li to F, therefore, we calculate the nuclear contribution using the core charge

$$Z_i = A_i - 2 \quad (\text{III.1})$$

where A_i is the atomic number. This procedure has been followed, for example, by Bloor and Maksic¹. Barfield et al.², however, compensate for the core electrons, differently. They treat them as doubly occupying an uncharged $1s$ orbital and add their contribution to that of the valence MO's; they then use the A_i directly in the nuclear term. However, at typical internuclear distances and using typical $1s$ - exponent values, we find that this procedure does not lead to significantly different core contributions than the point charge approximation used by us. At the oxygen centre in CO, for example, this results in a difference of about 0.003 a.u. in the final computed field gradient. The point charge model, we feel, is more in consonance with the spirit of the all-valence electron formalism used. We may note here that the EFG's reported in this thesis are all in atomic units, unless otherwise stated.

Table III.1

Bond distances (R in Å) used for the Linear Molecules
under study*

Molecule	Bond	R	Molecule	Bond	R
LiD	Li-D	1.5939	N ₂	N-N	1.094
DF	D-F	0.917	NCCN	N-C	1.150
DCN	D-C	1.066		C-C	1.380
	C-N	1.060	CO	C-O	1.128
DCCD	D-C	1.060			
	C-C	1.204			

*L.E. Sutton, "Tables of Interatomic Distances and Configurations in Molecules and Ions", The Chemical Society, London(1965).

In order to study the effect of inclusion of three-centre integrals on the computed field gradient in the approximate MO formalisms, we calculated the field gradients at the deuterium centre in DCN and DCCD and at the nitrogen centre in HCN using the three models chosen, namely CNDO/2, INDO and NN-INDO, arbitrarily setting all the three-centre integrals to zero. Our results from this calculation are compared with the results obtained with all three-centre integrals included in Table III.2. Kern and Karplus³ in their calculations using ab-initio wave functions have used the same procedure to evaluate the importance of three-centre integrals. It is seen that the effect is much more pronounced in the case of D than in the case of N; this is to be expected since in the nitrogen case one-centre contributions are the largest, whereas in the deuterium case the one-centre contributions are zero because of the symmetry of the 1s orbital. In the total field gradient, this effect will be magnified still further, since this is computed as a difference of the nuclear and electronic contributions which are of opposite sign and comparable in magnitude. Thus, we conclude that for deuterium the three centre contributions are quite significant, whereas for the first-row elements these are not so important. These conclusions are also supported by the earlier findings of Kern and Karplus³.

For the sake of completeness, we have performed computations reported in this thesis with the inclusion of all

Table III.2

Effect of Three-centre Integrals on Computed Electric Field Gradients
(the tabulated quantity is $-q_{elec}$ arising from valence electrons only)

Molecule*	CNDO/2			INDO			NN-INDO		
	Case 1	Case 2	% diff.	Case 1	Case 2	% diff.	Case 1	Case 2	% diff.
<u>DCN</u>	0.66852	0.59716	10.7	0.65207	0.58843	9.8	0.56599	0.45724	19.2
<u>HCN</u>	1.04301	1.01271	2.9	0.92510	0.89582	3.2	1.14919	1.12932	1.7
<u>DCGD</u>	0.63291	0.55146	12.0	0.62369	0.54526	12.5	0.53022	0.44223	16.6

* The nucleus in question is underlined

Case 1 - With three-centre integrals included

Case 2 - Without three-centre integrals

integrals. Since we interpret the NDO wave functions as being over an OAO basis set, the MO coefficient matrix has to be transformed so as to give the coefficient matrix over the overlapping AO basis set. The transformed coefficient matrix \underline{C} is obtained by the transformation

$$\underline{C} = \underline{C}' \underline{S}^{-\frac{1}{2}} \quad (\text{III.2})$$

In this equation \underline{C}' has row indices labelling MO's and column indices labelling OAO's. If the reverse convention is used, then eqn. (III.2) should be replaced by

$$\underline{C} = \underline{S}^{-\frac{1}{2}} \underline{C}' \quad (\text{III.3})$$

This process is referred to as 'deorthogonalisation'. All our calculations are done using the deorthogonalised MO coefficient matrix.

In order to analyse the contribution to the EFG's atomwise, we may write the expressions of the electronic contribution to the EFG as³

$$2 \sum_{i=1}^n \sum_{k=1}^M \sum_{l=1}^M C_{ki} C_{li} \langle \phi_k | q_{op} | \phi_l \rangle = \sum_{k=1}^M \{ 2 \sum_{i=1}^n [C_{ki}^2 \langle \phi_k | q_{op} | \phi_k \rangle + \sum_{l=1}^M C_{ki} C_{li} \langle \phi_k | q_{op} | \phi_l \rangle] \} \quad (\text{III.4})$$

where k, l are the indices over the deorthogonalised basis set AO's (M in number) and i is the index over the occupied molecular orbitals (n in number). The prime over the second summation

in the r.h.s. implies that terms with $k = 1$ are to be omitted. Now on the right hand side, the quantity within braces may be regarded as gross population weighted by the field gradient operator, q_{op} , of the k^{th} AO, i.e. the k^{th} AO contribution to the EFG. The overlap contribution is divided equally between the orbitals involved, so that the sum over all orbitals equals the total electric field gradient. Atomic orbital-wise contributions reported in this chapter have been calculated by this procedure. We do not present the electronic contributions MO-wise since there is no uniqueness about the MO's. It is well-known that MO's may be subjected to an orthogonal transformation leading to differing contributions orbital-wise. Further, large amounts of cancellations in the contributions to EFG's from various MO's do occur making the interpretation very difficult. In the following sections we present and analyse the results of our calculations on EFG's in terms of the nuclear sites, viz., 2H , 7Li , ^{14}N and ^{17}O in the molecules mentioned earlier.

III.2 EFG's at Deuterium Site in LiD, DF, DCN and DCCD

Table III.3 summarises our results on EFG's in the molecules LiD, DF, DCN and DCCD at the deuterium sites. We shall discuss these results now.

LiD

The total EFG values obtained using CNDO/2, INDO, and NN-INDO methods are all seen to be higher than the experimental

Table III.3

MFG's at the Deuterium Site in LiD, DF, DCN, and DCCD

Molecule		CNDO/2	INDO	NN-INDO	Expt.
LiD	Nuc.	0.07319	0.07319	0.07319	
	Elec.	-0.01050	-0.00967	-0.00272	
	Tot.	0.06269	0.06352	0.07047	0.0491 ^(a)
DF	Nuc.	2.69033	2.69033	2.69033	
	Elec.	-2.19764	-2.23234	-2.05927	
	Tot.	0.49269	0.45799	0.63066	0.5270 ^(b)
DCN	Nuc.	1.13280	1.13280	1.13280	
	Elec.	-0.66862	-0.65207	-0.56599	0.3009 ^(c)
	Tot.	0.46418	0.48073	0.56681	
DCCD	Nuc.	1.10553	1.10553	1.10553	
	Elec.	-0.63291	-0.62369	-0.53022	
	Tot.	0.47262	0.48184	0.57531	0.2976 ^(d)

(a) See Ref. 4

(b) See Ref. 21

(c) See Ref. 26

(d) See Ref. 27 & 28.

value of 0.0491 of Wharton, Gold and Klemperer⁴ using the molecular beam magnetic resonance method. However, they are quite close to the theoretical values of 0.0574, 0.0694 and 0.0683 obtained by Kolker and Karplus⁵, from the three different levels of ab initio SCF MO wave functions of Ransil⁶. Kahalas and Nesbet⁷ reported a value of 0.0549 using STO's and elliptic orbitals. Browne and Matsen⁸ using valence bond functions and an internuclear distance of 1.6 Å obtained a value of 0.0500 after averaging over the molecular vibrational motion. Bender and Davidson⁹ using a 45-term wave function obtained a value of 0.0466. The core model calculations of Avgeropoulos and Ebbing¹⁰ gave values of 0.0430 without vibrational averaging. Arrighini et al.¹¹ who performed a SCF MO with CI at the Hartree-Fock level obtained a value of 0.0595. Ditchfield et al.¹² using gaussian orbitals report a range of values from 0.0683 to 0.0695 depending on the type of wave function used. Docken and Hinze¹³ using the multi-configuration SCF (MCSCF) method obtained values of 0.0493 and 0.0488 respectively before and after vibrational averaging, over the ground vibrational state. At the semi-empirical level, the calculations of Barfield et al.² yielded a value of 0.0595 by the INDO method as against our value of 0.0635 by the same method; the difference is due mainly to the fact that they treat the 1s core on Li differently as discussed earlier. These authors using the optimised STO exponents of Hehre, Stewart and Pople¹⁴ obtain a value of 0.0522. However,

their use of the original INDO parameters together with modified exponents is not entirely consistent. On the other hand, their study confirms the importance of the role that orbital exponents play in EFG calculations. In our studies, the NN-INDO formalism using Burns exponents (which are lower than Slater values) is seen to under-estimate the numerical value of the electronic contribution to the field gradient, thereby leading to a larger value of EFG in comparison with the values obtained from the CNDO/2 and INDO methods. It will be seen that the results of these latter two methods, both of which employ Slater exponents, are close to each other. The use of optimised exponents of Hehre, Stewart and Pople (generally higher than Slater values) leads to a value of EFG lower than that obtained using the Slater exponents. The correlation seems to be unmistakable in this case.

DF

Our values using the NN-INDO wave function (see Table III.3) are close to the ab initio SCF MO results of Kolker and Karplus⁵ viz. 0.6278, using Ransil's MO function which employs Slater's exponents. The CNDO/2 and INDO values are much lower than that of NN-INDO as was found earlier in the case of LiD. Bloor and Maksic¹ using the CNDO/2 wave function after deorthogonalisation obtained a value of 0.519 compared to our value of 0.4927, the difference being due to the different inter-nuclear distance value. Bloor and Maksic also report a value of 0.580 from their self-

consistent charge (SCC) model calculation. The INDO value obtained in the present work agrees with that of Barfield et al.² who report a value of 0.4584. At the ab initio level several calculations are available^{12,15-20}. These theoretical results range from 0.54 to 0.757 and employ different types of ab initio wave functions. On the experimental side, Muentert and Klemperer²¹ have obtained a value of 0.5270 from their molecular beam electric resonance study. It is thus seen that the EFG results obtained from the three semi-empirical MO formalisms are all rather satisfactory.

DCN

The calculated values at the CNDO/2 and INDO levels (see Table III.3) are comparable with the results of Kern and Karplus³, namely, 0.472, using Slater exponents. McLean and Yoshimine's unpublished result quoted by O'Konski and Ha²² is 0.317. O'Konski and Ha using Gaussian Lobe orbitals (GLO) obtained a value of 0.365. Harrison²³ has also employed GLO's to calculate the EFG's and has obtained a value of 0.3827. Ditchfield et al.¹² using gaussian functions obtained values ranging from 0.472 to 0.480. Snyder and Basch^{24,25} using a wave function of double zeta quality obtain a value of 0.3687. At the semi-empirical level Bloor and Maksic report a value of 0.481 using CNDO/2 whereas Barfield and coworkers² using the INDO method report a value of 0.4792 with Slater exponents. Our CNDO/2 and INDO results substantially agree with the values of

Bloor and Maksic and Barfield et al. Use of Hehre-Stewart-Pople orbital exponents in INDO has been shown by Barfield et al. to yield a value of 0.410. The best available experimental value²⁶ appears to be 0.3009. Most of the ab initio as well as semi-empirical results are seen to be higher than the experimental value. The NN-INDO value, in particular, is higher than the CNDO/2 and INDO values. In the light of our earlier comments in the LiD case, we may conclude that Burns exponents do not appear to be optimal for EFG calculations.

DCCD

Our calculations by the CNDO/2 and INDO methods (see Table III.3) give values comparable to the ab initio 'Best Atom Molecular Orbital' (BAMO) result of Kern and Karplus³, viz., 0.473. The NN-INDO result is higher. Harrison²³ employed GLO's and obtained a value of 0.3899. Ditchfield et al.¹² using gaussian orbitals report values ranging from 0.473 to 0.483 depending on the wave function employed. Snyder and Basch¹⁸ using a wave function of double zeta quality report a value of 0.3854. The experimental deuterium quadrupole coupling constant of Pinkerton²⁷ from molecular beam study leads to the value of 0.2976. This value is not very different from that reported by Millet and Dailey²⁸ who used, the liquid crystal NMR method. Bloor and Maksic's¹ CNDO/2 value of 0.473 and Barfield's² INDO value of 0.485 using Slater exponents are in excellent agreement with ours. With the use of Hehre-Stewart-Pople exponents, Barfield reports a lower value of 0.447 in the

INDO formalism. As in the earlier cases the NN-INDO formalism leads to a higher EFG value at the deuterium site. This appears to be a consequence of the use of Burns exponents.

III.2.1 Next-Neighbour Contribution to EFG's in DCN and DCCD

We shall now discuss the atomwise contribution to EFG in DCN and DCCD and analyse the importance of next-neighbour contribution at the deuterium site. The atomic orbitalwise contribution to the EFG's in DCN and DCCD at the D site are presented in Tables III.4 and III.5 respectively. To see clearly, the importance of next-neighbour contribution, the contribution from D and the neighbouring C alone are summed and presented along with the total EFG's in Table III.6. The total EFG values and the partial sum values are easily seen to be close to each other. These trends parallel the findings of Kern and Karplus³, and Snyder²⁰. However, the numbers presented in Table III.6 should be viewed qualitatively rather than quantitatively, since the orbitalwise analysis on which they are based is somewhat arbitrary in the partitioning of the overlap contribution. In a few of the tabulated instances it is seen that the partial sum of the self- and next-neighbour contributions marginally exceeds the total. This is, however, compensated by contributions of opposite sign from the remaining terms in the total EFG. It is clear that for the deuterium site, the main contribution to EFG arises from the near neighbour atom. The near constancy in the EFG value at the deuterium site in DCN and DCCD can be thus understood.

Table III.4

Atomic Orbitalwise Contribution to EFG in DCN at D Site

Contributions from	CNDO/2	INDO	NN-INDO
Deuterium [#] :			
1s	-0.06228	-0.06030	-0.03604
Carbon :			
2s	-0.15850	-0.16087	-0.15089
2p	-0.15216	-0.13972	-0.09260
2p	-0.15417	-0.13696	-0.12473
Tot. $q_{elec.}$	-0.45483	-0.43755	-0.36822
$q_{nuc.}$	0.97860	0.97860	0.97860
Nitrogen			
2s	-0.04025	-0.04214	-0.04190
2p	-0.06446	-0.06520	-0.06310
2p	-0.04678	-0.04687	-0.06213
Tot. $q_{elec.}$	-0.15149	-0.15421	-0.16714
$q_{nuc.}$	0.15420	0.15420	0.15420
q_{total}	0.46418	0.48073	0.56681

[#] The nuclear contribution to EFG from Deuterium is zero.

Table III.5

Atomic Orbitalwise Contribution to EFG in DCCD at D Site*

Contributions from	CNDO/2	INDO	NN-INDO
Deuterium 1#:			
1s	-0.06228	-0.06136	-0.04320
Carbon 1 :			
2s	-0.16065	-0.16489	-0.15137
2p	-0.14938	-0.14958	-0.10470
2p	-0.14881	-0.13790	-0.12290
Tot. $q_{elec.}$	-0.45884	-0.45237	-0.37897
$q_{nuc.}$	0.99530	0.99530	0.99530
Carbon 2 :			
2s	-0.02807	-0.02840	-0.03254
2p	-0.05098	-0.05098	0.04644
2p	-0.02478	-0.02306	-0.02332
Tot. $q_{elec.}$	-0.10383	-0.10238	-0.10016
$q_{nuc.}$	0.10215	0.10215	0.10215
Deuterium 2 :			
1s	-0.00747	-0.00753	-0.00635
$q_{nuc.}$	0.00807	0.00807	0.00807
q_{total}	0.47262	0.48184	0.57531

*EFG values shown are orbital contributions at the deuterium labelled D_1 from the two carbons (C_1 & C_2) and the other deuterium D_2 .

The nuclear contribution to EFG from Deuterium 1 is zero.

Table III.6

Next Neighbour Contributions to EFG's

		DC				D ₁ C ₁ C ₂ D ₂			
		Contribution for D and C= q _{partial} (Elec.+Nuc.)	q _{total}	q _{total} /q _{partial}	Contribution from D ₁ and C ₁ =q _{partial} (Elec.+Nuc.)	q _{total}	q _{total} /q _{partial}		
CNDO/2	0.46149	0.46418	1.00583	0.47388	0.47262	0.99734			
INDO	0.48075	0.48073	0.99996	0.48157	0.48184	1.00056			
NW-INDO	0.57434	0.56681	0.98689	0.57313	0.57531	1.00380			

III.3 EFG at Lithium Site in LiD

Our values for the EFG at the Li site by the CNDO/2, INDO and NN-INDO method are -0.04768, -0.04558 and -0.03308. Kolker and Karplus⁵ report a value of -0.04012 using the BAMO wave function of Ransil⁶. Browne and Matsen⁸ calculated a value of -0.0346 from their ab initio wave function while Cheng and Byers-Brown²⁹, who extended the work of Browne and Matsen, obtained a similar result. Ditchfield et al.¹² using gaussian orbitals obtained values ranging from -0.0206 to -0.0259. Arrighini, Guidotti and Tomasi¹¹ using eleven STO's and configuration interaction obtained a value of -0.0429. S.Green³⁰, who made a CI calculation with 200 configurations obtained a value of -0.0429. Docken and Hinze¹³ using multiconfiguration SCF method obtained a value of -0.0399 without vibrational correction.

The experimental value of Wharton et al.⁴ using molecular beam resonance technique, is 0.0402. It may be noted here that ours are the first calculations on ⁷Li EFG at the semi-empirical level, which include all integrals. In comparing our results on ⁷Li using the three different semi-empirical MO formalisms, we see that the NN-INDO method leads to a lower value. The reason for this is, that the one-centre contribution to EFG is underestimated due to the use of Burns exponents.

III.4 EFG's at Nitrogen Centre in N_2 , HCN and NCCN

The EFG values obtained in the present work for the nitrogen centre in N_2 , HCN and NCCN are presented in Table III.7. For N_2 and HCN, the orbitalwise contributions to the EFG are also reported in Tables III.8 and III.9 respectively.

N_2

In N_2 , Richardson's calculations³¹ using Ransil's wave function⁶ suggested that the electronic contribution to EFG from the other nitrogen is nearly cancelled by the nuclear contribution. This, however, is not observed in the present calculations (see Table III.8), in any of the three models used. The widest discrepancy occurs in the case of NN-INDO. Partial cancellation of contributions from the nitrogen p_σ and p_π orbitals leads to a smaller overall contribution at that nitrogen centre. Richardson obtained values of -0.310 and -1.341 respectively using Ransil's BAMO and BIMO wave functions. The sensitivity of EFG values to the choice of wave function is marked in this case. The result of O'Konski and Ha²² using gaussian lobe basis is -1.086. Dunning³², using the SCF MO wave functions with various basis contractions giving the best energy, calculated, a value of -1.3574. Ditchfield et al.¹² obtained values varying from -0.137 to -0.319 depending upon the nature of the gaussian wave function used. The experimental value available from NQR studies³³ on solid N_2 at 4.2K corresponds to a value of -1.0254.

Table III.7

EFG's at Nitrogen Centre for N_2 , HCN and NCCN

Molecule		CNDO/2	INDO	NN-INDO	Expt.
N_2	Elec.	-1.36501	-1.27525	-1.54068	
	Nuc.	1.13171	1.13171	1.13171	
	Tot.	-0.23330	-0.14354	-0.40893	-1.0254 ^(a)
HCN	Elec.	-1.04301	-0.92510	-1.14919	
	Nuc.	1.02615	1.02615	1.02615	
	Tot.	-0.01686	0.10105	-0.12304	-1.010 ^(b)
NCCN	Elec.	-0.97046	-0.87565	-1.28242	
	Nuc.	0.88237	0.88237	0.88237	
	Tot.	-0.08809	0.00672	-0.40005	-0.9416 ^(c)

(a) See Ref. 33

(b) See Ref. 37

(c) See Ref. 38

Table III.8

Atomic Orbitalwise Contributions to EFG in N_2 at N Site

Contributions from	CNDO/2	INDO	NN-INDO
Nitrogen 1 :			
2s	0.02765	0.04889	-0.03827
2p	1.57524	1.57524	0.90356
2p	-2.12688	-2.04692	-1.80101
Tot. $q_{elec.}$	-0.53399	-0.42279	-0.93572
$q_{nuc.}$	0.0	0.0	0.0
Nitrogen 2 :			
2s	-0.23438	-0.24128	-0.15871
2p	-0.14584	-0.14584	-0.08534
2p	-0.46100	-0.46533	-0.36090
Tot. $q_{elec.}$	-0.84122	-0.85245	-0.60495
$q_{nuc.}$	1.13171	1.13171	1.13171
q_{total}	-0.23330	-0.14354	-0.40896

Table III.9

Atomic Orbitalwise Contributions to EFG in HCN at N Site

Contributions from	CNDO/2	INDO	NN-INDO
Nitrogen :			
2s	0.03730	0.04940	0.02560
2p	1.62468	1.65350	1.03424
2p	-2.09931	-2.03953	-1.88288
Tot. $q_{elec.}$	-0.43733	-0.33663	-0.82304
$q_{nuc.}$	0.0	0.0	0.0
Carbon :			
2s	-0.24293	-0.25073	-0.16177
2p	-0.05476	-0.05240	-0.00924
2p	-0.28302	-0.26069	-0.08863
Tot. $q_{elec.}$	-0.58071	-0.56382	-0.25964
$q_{nuc.}$	-0.99530	0.99530	0.99530
Hydrogen :			
1s	-0.02496	-0.02464	-0.01531
$q_{nuc.}$	0.03084	0.03084	0.03084
q_{total}	-0.01686	0.10105	-0.12304

A value of -1.223 has been quoted by O'Konski and Ha²² and presumably this corresponds to the NQR data on solid N_2 at a different temperature. In comparing all the available ab initio values it is found that use of BLMO wave function of Ransil and the Dunning wave function yield results closest to experiment. This observation signifies the importance of properly chosen orbital exponents in calculating EFG's. At the semi-empirical level the NN-INDO value of -0.4005 is seen to be a significant improvement on the CNDO/2 and INDO values.

HCN

In HCN, the value obtained by Kern and Karplus³ is -0.481 . McLean and Yoshimine³⁴ reported a value of -1.204 from their ab initio calculations. O'Konski and Ha²² obtained a value of -0.854 with the extended GIO basis set. Bonaccorsi, Scrocco and Tomasi³⁵, using 54 STO's reported a value of -1.1948 . Ditchfield et al¹² quote values ranging from -0.322 to -0.481 from their ab initio calculations using gaussian orbitals. Very recently Barber et al³⁶ obtained a value of -1.14313 using Dunning's sp basis set. To our knowledge at the semi-empirical level ours is the first calculation of EFG at ^{14}N site in HCN including all integrals. The CNDO/2 value (see Table III.7) is extremely low while the INDO value is positive and hence of wrong sign. The experimental value³⁷ is -1.010 . The NN-INDO procedure is again seen to improve upon the performance of CNDO and INDO. A closer analysis of

the cause for the lower values obtained by the CNDO/2 and INDO methods will be now made. Table III.9 analyses the situation in terms of the atomic orbital contributions to the EFG at the nitrogen site in this molecule. It will be seen that in CNDO/2, the total contribution from the nitrogen centre is nearly cancelled by that from the carbon centre. In INDO, the contribution from the carbon centre is even larger than that from the nitrogen centre itself and thereby yields a positive EFG value. On the other hand, the NN-INDO procedure yields atomic orbital contributions which are more reasonable.

NCCN

In the case of cyanogen molecule, our results (see Table III.7) again reflect the same trend as in HCN. CNDO/2 yields a small negative value; INDO gives an even smaller but positive value; NN-INDO gives a negative value about one-third the ab initio result of Bonaccorsi, Scrocco and Tomasi³⁵. These authors used a SCF MO with 64 STO's in their ab initio calculations. Very recently, Barber et al.³⁶ made an ab initio calculation using the Dunning sp basis set and reported a value of -1.13718. The solid state NQR experimental data of Haigh and Guibe³⁸ leads to a value of -0.9416. Amongst the three semi-empirical methods employed here, the NN-INDO formalism appears to be more satisfactory for the EFG at the nitrogen site.

Before concluding this discussion on the EFG's at the nitrogen sites in these molecules, it may be pointed out here, that Dewar et al.³⁹ have calculated the EFG's by their MINDO/3 method for a number of nitrogen containing molecules including N₂, HCN and NCCN. Unfortunately, these authors did not evaluate the two- and three-centre integrals exactly and hence no meaningful comparison is possible between our results and theirs.

III.5 ¹⁷O Field Gradient in CO

The atomic orbitalwise analysis of the EFG at ¹⁷O site in this molecule is presented in Table III.10 along with the total EFG values.

Richardson³¹ has obtained a value of -0.151 from an ab initio calculation. However, an approximate procedure was employed by him in the evaluation of the integrals. Later, Scrocco⁴⁰ reported a value of -0.16 using Ransil's⁶ wave functions while Nesbet⁴¹, who used a wave function of double zeta quality with polarisation, obtained a value of -0.627. Lefebvre-Brion et al.⁴² and Huo⁴³ obtained with SCF MO procedures, values in the range of -0.621 to -0.679. McLean and Yoshimine¹⁶, using Slater functions in the Hartree-Fock procedure, obtained a value of -0.724. The work of Neumann and Moskowitz⁴¹ has yielded a value of -0.697. These authors employed an extended gaussian basis set. Snyder and Basch¹⁸ using a SCF wave function of double zeta quality obtained a value of -0.3029. Comparing this value with that of Nesbet brings out clearly the importance of inclusion of

Table III.10

Atomic Orbitalwise Contribution to EFG in CO at ^{17}O Site

Contributions from	CNDO/2	INDO	NN-INDO
Oxygen :			
2s 2s	0.01343	0.02287	-0.02269
2p	3.96680	3.88786	2.98330
2p	-4.20681	-4.31376	-3.62852
Tot. $q_{\text{elec.}}$	-0.22656	-0.40303	-0.86791
$q_{\text{nuc.}}$	0.0	0.0	0.0
Carbon :			
2s	-0.16080	-0.15640	-0.07963
2p	-0.00066	-0.00300	0.02554
2p	-0.33331	-0.32192	0.19097
Tot. $q_{\text{elec.}}$	-0.49477	-0.48132	-0.24486
$q_{\text{nuc.}}$	0.82550	0.82550	0.82550
q_{total}	0.10417	-0.05885	-0.28748

polarisation functions. Recently, Amos⁴⁵ made a SCF-CI calculation of the EFG at the ^{17}O site in CO and studied its vibrational dependence also. The EFG value drastically changes from -0.6332 to -0.8436 with the inclusion of configuration interaction in the SCF MO wave function. The experimental value of -0.7168 due to Lovas and Tiemann⁴⁶, is in good agreement with the recent ab initio results. At the semi-empirical level, ours is perhaps the first calculation that includes one- and two-centre integrals. The NN-INDO result is very close to that of Snyder and Basch and is better than the CNDO/2 and INDO results.

III.6 Some Comments on the Role of Orbital Exponents in EFG Calculations

The tendency of NN-INDO to yield values of total EFG numerically higher than the other two NDO schemes is amply clear from the present work. This has its origin mainly in the use of AO's with exponents derived from Burns rules rather than Slater rules. Burns rule AO's are generally more spread out than the STO's. Whitehead⁴⁷ compares the effect of Burns exponents in a molecule such as HF with that of Slater exponents and the BLMO exponents, and finds that the Burns exponents tend to accumulate charge in the inter-nuclear region near F, giving rise to a numerically low value for the electronic field gradient for the H site. Our results on linear molecules, also show that the NN-INDO method, using Burns exponents, does give too low an electronic field gradient at the H site; however, the electronic

contribution at the other nuclear sites in the molecules examined here is uniformly higher in NN-INDO as compared to CNDO/2 and INDO, the sole exception being LiD. The explanation for this lies in the fact, that with the greater 'expansion' of the orbitals, the two-centre terms tend to become more important.

III.7 Empirical Evaluations of EFG's Using Electronic Populations on the Atom with the Quadrupolar Nucleus

Several empirical methods⁴⁸ for the calculation of EFG's have their basis in the fact that the one-centre integrals are far larger than the two-centre or three-centre integrals. For atoms other than hydrogen, neglecting contribution from cores, and assuming that other atom contributions and the nuclear contributions cancel each other, leads to⁴⁹ the equation

$$q = q^0 \left(n_z - \frac{n_x + n_y}{2} \right) \quad (\text{III.5})$$

where q^0 is the EFG due to a single p_z electron at the site of the nucleus, and n_x , n_y and n_z are the populations in the p_x , p_y and p_z orbitals on the atom in question. This equation, or the related one obtained by multiplying throughout by eQ , forms the basis for the empirical evaluation of QCC's or EFG's.

We shall briefly examine here the validity of this type of approach, using our MO data on the molecules containing ^{14}N and ^{17}O nuclei. Clearly, this approach is meaningless for deuterium couplings. Two kinds of populations are generally employed in eqn. (III.5). These are the 'net' and 'gross' populations⁵⁰. In connection with the CNDO/2 and related methods,

there is the question of the nature of the orbital basis, too. If the CNDO function is interpreted as being over an OAO basis, then with Betsuyaku⁵¹, we have to use the elements of the charge density-bond order matrix over the deorthogonalised basis and use the populations thus obtained in the above formula. In principle, we have to take the gross population over the overlapping basis for the calculations. More commonly, the net population from the calculation over the orthogonal basis has been used. This is unsatisfactory, since net populations over OAO's have components of other orbitals in them and the procedure effectively introduces many-center contributions. q^0 in eqn. (III.5) thus loses its atomic significance.

There does not appear to be a unique value of q^0 for each atom. Literature values⁵² of q^0 for nitrogen, for example, range from -7.4 to -14.0. In the present calculations, we have adopted the q^0 values obtained from the $\langle 1/r^3 \rangle$ values estimated by Barnes and Smith⁵³ from atomic spectral data. This choice is made because it is independent of any reference compound. Our q values have been computed using four different schemes over OAO basis functions using net and gross populations. The results are presented in Table III.11 for the three semi-empirical MO formalisms chosen. On comparing the empirical q data with experiment, there does not appear to be a clear correlation. Indeed, recently Barber et al.³⁶, based on their ab initio SCF calculations on some nitrogen containing molecules, have also noted that there is

Table III.11

Semi-empirical evaluation of EFG's in Some Linear Molecules
using Populations
(Nucleus of interest is indicated by an asterisk)

Formalism	Basis [#]	Population type	$\text{N}\equiv\text{N}^*$	$\text{HC}\equiv\text{N}^*$	$\text{N}\equiv\text{C}-\text{C}\equiv\text{N}^*$	$\text{C}\equiv\text{O}^*$
CNDO/2	I	Net	-0.620	-0.726	-0.624	-0.394
		Gross	-0.900	-0.754	-0.822	-0.700
	II	Net	-0.297	-0.243	-0.147	-0.038
		Gross	-0.398	-0.419	-0.397	-0.229
INDO	I	Net	-0.541	-0.648	-0.560	-0.498
		Gross	-0.831	-0.690	-0.774	-0.774
	II	Net	-0.219	-0.157	-0.072	-0.263
		Gross	-0.287	-0.332	-0.328	-0.337
NN-INDO	II	Net	-1.283	-1.341	-1.207	-1.327
		Gross	-1.089	-1.007	-1.010	-1.829
Exptl.			-1.025 (a)	-1.131 (b)	-0.942 (c)	-0.728 (d)

I indicates without deorthogonalisation and II indicates with deorthogonalisation

(a) See Ref. 33

(b) See Ref. 37

(c) See Ref. 38

(d) See Ref. 46

no evidence for any correlation between ^{14}N EFG's and Mulliken population analysis indices. The situation might not be different in the case of other nuclei as well. Hence, in our opinion, for a quantitative evaluation of the merits and demerits of the various MO wave functions, with regard to the prediction of EFG's, empirical methods based on population are unsatisfactory. One must therefore, evaluate directly the expectation value of the EFG operator over the MO wave functions, as we have done here.

In the next two chapters, we present our EFG results at the ^2H , $^{10,11}\text{B}$, ^{14}N and ^{17}O sites in several non-linear molecules.

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CHAPTER IV

EFG'S AND ASYMMETRY PARAMETERS IN SOME NON-LINEAR MOLECULES

IV. 1 General

With the exception of symmetric top molecules, the principal axis of the EFG tensor need not coincide with the molecular symmetry axis of non-linear molecules. Therefore, it is necessary to evaluate the off-diagonal and diagonal elements of the EFG tensor. Now, by the Laplace equation two of the diagonal components uniquely determine the third, and as the EFG tensor is symmetric, only three off-diagonal elements are independent. Hence, a total of five EFG components are required to describe the tensor completely. The EFG tensor can then be diagonalised by a similarity transformation

$$\underline{C} \underline{q} \underline{C}^{-1} = \underline{q_d} \quad (\text{IV.1})$$

From the diagonal EFG tensor $\underline{q_d}$, the principal component and the asymmetry parameter are calculated. In order to define the orientation of the EFG principal axis system with respect to the molecule-fixed coordinate system we further need the direction cosines and these are obtained as elements of the transformation matrix \underline{C} .

$$C_{ij} = \cos(u_i, v_j); (i, j=1, 2, 3). \quad (\text{IV.2})$$

where u_1, u_2 and u_3 refer to the molecule-fixed coordinate system and v_1, v_2 and v_3 refer to the EFG principal axis system. It is customary to represent such a rotational transformation of coordinates by using Euler angles connecting the two systems. Even though, such a procedure is more elegant, in

this thesis we have chosen to represent the EFG tensor components in terms of angles relative to the various bond directions; this method has the advantage of easier visualisation and interpretation from chemical point of view.

We follow the convention of defining the EFG principal components q_{xx} , q_{yy} and q_{zz} such that

$$|q_{zz}| > |q_{yy}| > |q_{xx}| \quad (\text{IV.3})$$

and the asymmetry parameter as

$$\eta = \frac{|q_{yy} - q_{xx}|}{|q_{zz}|} \quad (\text{IV.4})$$

so that η is always a positive real number between 0 and 1.

The molecules we have chosen for study in this chapter are the acyclic molecules CD_4 , ND_3 , D_2O , N_2D_4 and D_2CO and the cyclic molecules furan and pyrrole. All our EFG calculations reported here have been done with the experimental geometry, obtained from the literature, preferring microwave data wherever available. The geometries used are indicated in Fig. IV.1. The results of CNDO/2, INDO and NN-INDO investigations on the EFG's on these molecules are presented and discussed in the following sections.

IV.2 EFG's in Some Acyclic Molecules

We shall now consider the field gradients at the D site in CD_4 , ND_3 , D_2O , N_2D_4 and D_2CO , the N site in ND_3 and N_2D_4 , and the O site in H_2O and H_2CO .

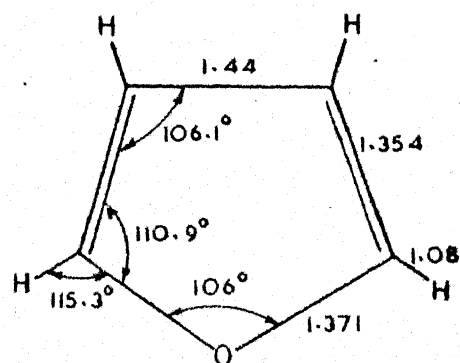
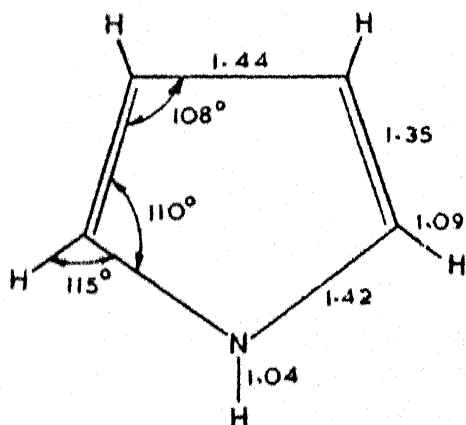
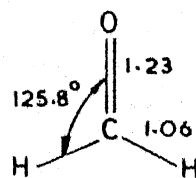
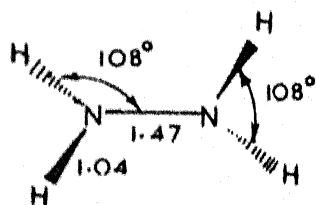
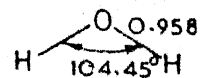
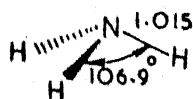
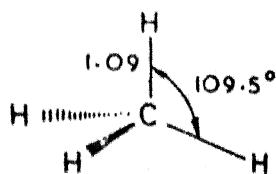


FIG. IV-1. GEOMETRY OF THE MOLECULES STUDIED

IV.2.1 Deuterium Field Gradients

The results obtained using the CNDO/2, INDO and NN-INDO schemes for the principal component and asymmetry parameter for the D-sites mentioned above are listed in Table IV.1. As has been already observed in Chapter III, the values obtained for deuterium field gradients by the NN-INDO procedure are higher than that from the other two methods.

CD₄

Our CNDO/2 and INDO calculations agree with Bloor and Maksic's¹ value of 0.393 and Barfield et al.² 0.409, respectively. Arrighini et al.³ using 39 STO's in the ab initio SCF MO calculation obtained a value of 0.316. Later Franchini et al.⁴ improved upon this calculation by using strongly orthogonal geminals and obtained a value of 0.324. Snyder and Basch⁵ (see also Snyder⁶) used STO's of double zeta quality in their ab initio calculations and obtained a value of 0.3362. Dixon, Claxton and Overill⁷ optimised the C-H bond distance and the orbital exponent on D and reported values ranging from 0.3405 to 0.304 for exponents ranging from 1.3 to 1.5 at an inter-nuclear distance of 1.95 bohr. Bendazzoli, Dixon and Palmieri⁸ using 18 STO's report a value of 0.349. Dixon⁹ using double zeta, and other gaussian wave functions reported values ranging from 0.306 to 0.352. Eberhardt, Moccia and Zandomeneghi¹⁰ using 39 STO's and configuration interaction involving all single and double

Table IV.1
EPG's at D Sites

Molecules	CNDO/2		INDO		NN-INDO	
	q_{zz}	η	q_{zz}	η	q_{zz}	η
CD ₄	0.39608	0.0	0.40869	0.0	0.53256	0.0
ND ₃	0.47630	0.10	0.46706	0.10	0.70421	0.11
D ₂ O	0.48897	0.13	0.46400	0.14	0.67370	0.10
N ₂ D ₄	0.45765	0.19	0.44086	0.20	0.61006	0.24
D ₂ CO	0.36432	0.009	0.38208	0.007	0.49804	0.004

excited configurations of "A" symmetry obtained a value of 0.3205. The molecular beam electric resonance experiments of Wofsy et al.¹¹ lead to a deuterium QCC value of 192 KHz, corresponding to an EFG value of 0.286 a.u. The experimental asymmetry parameter value is zero and is in agreement with all the reported theoretical calculations. However, the experimental q value is lower than all the values theoretically calculated. The CNDO/2 and INDO values are lower than the NN-INDO value. This feature of NN-INDO was also noticed earlier with other deuterium EFG's (vide Chapter III).

ND₃

Our CNDO/2 results agree substantially with Bloor and Maksic's calculations¹. These authors report a value of 0.393 for q_{zz} , and $\eta = 0.10$. Their value for the angle between the N-H bond direction and the principal axis of the EFG tensor is 2.9° . Our INDO calculation gives for this angle the value of 2.1° , and with the NN-INDO method the EFG principal axis almost coincides with the N-H bond. The INDO results of Barfield et al.² using the Slater orbital exponents, are $q_{zz} = 0.464$ and $\eta = 0.12$. Our INDO η value is slightly lower (0.10). Barfield et al. obtain a η value of 0.08 using Hehre-Stewart-Pople orbital exponents. Franchini et al.⁴, using 29 STO functions in their ab initio calculations, obtained values of $q = 0.4286$ and $\eta = 0.152$. Using 28 localised geminals these authors reported values of $q = 0.4234$ and $\eta = 0.149$. Kari and Csizmadia¹², using

a GTO basis, quote values of $q = 0.4331$ and $\eta = 0.133$. With configuration interaction involving 918 configurations, Kari and Csizmadia obtained $q = 0.4363$ and $\eta = 0.128$. Snyder and Basch⁵ (See also Snyder⁶) obtained using double zeta basis values of $q = 0.459$ and $\eta = 0.127$. Bendazzoli et al.⁸ quote values of $q = 0.457$ and $\eta = 0.120$, with their STO double zeta functions (See also Dixon⁹). Cook and Ebbing¹³ with their 'core' model calculation obtained values of $q = 0.4977$ and $\eta = 0.09$. Goddard et al.¹⁴, using basis sets which incorporated the conjugate gradient optimised N-atom basis, obtained after optimisation and scaling a value not very different from that of Kari and Csizmadia¹². The experimental values due to Cederberg¹⁵ are $q = 0.308$ and $\eta = 0.072$. Reviewing all the calculations in the light of this data, we see that the q -value has been overestimated by semi-empirical as well as ab initio formalisms. As far as the NN-INDO method is concerned it gives a higher value than CNDO/2 and INDO.

D₂O

Our results on D₂O by the INDO method and Barfield et al.'s² value of $q_{zz} = 0.474$ and $\eta = 0.14$, agree fairly well. Bloor and Maksic¹ do not quote any CNDO/2 values on D₂O, but using the self-consistent charge method they report a q_{zz} value of 0.534 and η value of 0.10. The principal axis obtained by our CNDO/2 calculation lies in the molecular plane and makes an angle of 2.75° with the O-D bond direction. In the INDO

calculations the value of this angle is 2.4° . In the NN-INDO the q_{zz} axis practically coincides with the O-H bond. Kern and Matcha¹⁶ studied the effect of vibrational corrections to the q in water. Franchini, Moccia and Zandomeneghi⁴ report using 27 STO's $q = 0.5413$, $\eta = 0.1183$; using strongly orthogonal geminal basis they reported values 0.5520 and 0.1145 respectively for q and η . Ermler and Kern¹⁷ with a GTO basis obtained $q = 0.502$ and $\eta = 0.138$ with vibrational corrections and $q = 0.564$ and $\eta = 0.127$ without vibrational corrections. Krohn, Ermler and Kern¹⁸ report $q = 0.569$ and $\eta = 0.129$ with vibrational corrections. Bendazzoli, Dixon and Palmieri⁸ using STO double zeta basis report $q = 0.576$ and $\eta = 0.111$; with GTO basis their values are 0.547 and 0.115 respectively (See also Dixon⁹). Schaefer¹⁹ has discussed some of the ab initio calculations on EFG's at the deuterium site in water in terms of the quality of the wave functions. Snyder and Basch⁵ report EFG components, from their double zeta quality STO MO wave functions, which lead to q_{zz} and η values, 0.5616 and 0.115 respectively. Rosenberg and Shavitt²⁰ obtain $q = 0.5625$ and $\eta = 0.115$ using a double zeta basis with polarisation. On the experimental side, Bluyssen, Verhoeven and Dymanus²¹ have reported values of 0.458 and 0.14 for q and η respectively. It is gratifying to see that both CNDO/2 and INDO values are in good agreement with the experimental values. The NN-INDO again gives too large a q value but a reasonable value for η .

N₂D₄

Our results are based on a conformation where the two ND₂ groups are staggered with respect to each other. Snyder and Basch⁵ (See also Snyder⁶) used a different conformation in their SCF MO calculations and obtained q values of 0.4274 and 0.425 for the two deuterium sites and η values of 0.104 and 0.141 respectively. Comparing our q values with those of Snyder and Basch we see that the CNDO/2 and INDO values are in reasonable agreement while the NN-INDO gives too high a value. With our geometry we find that the diagonalised EFG tensor has a principal axis, which although does not coincide exactly with the N-D bond lies within 1° of it. To our knowledge, no experimental data on the EFG's at the deuterium sites are available.

D₂CO

Our CNDO/2 values on D₂CO agree well with Bloor and Maksic's CNDO/2 value of 0.364 for q and 0.008 for η . Barfield et al.'s INDO results² on this molecule are based on the Hehre-Stewart-Pople orbital exponents. The values obtained by Barfield et al. in this manner are $q = 0.375$ and $\eta = 0.01$. The agreement with our INDO values using Slater exponents is reasonable. Neumann and Moskowitz²² using contracted geminal functions obtain $q = 0.262$ and $\eta = 0.157$. Snyder and Basch⁵ using SCF MO wave functions of double zeta quality have obtained $q = 0.286$ and $\eta = 0.007$. Garrison et al.²³ have reported components of q

Table IV.2
EFG's at N Sites

Molecules	CNDO/2		INDO		NN-INDO	
	q_{zz}	η	q_{zz}	η	q_{zz}	η
NH ₃	-1.45798	0.0	-1.59082	0.0	-1.460140	0.0
N ₂ H ₄	0.95222	0.026	0.88208	0.163	-1.17287	0.214

for a gaussian basis. On diagonalisation, the values we obtain are $q = 0.21964$ and $\eta = 0.184$. . This η value appears to be too large. Experimentally Flygare²⁴ obtained a value of 0.2622 for the field gradient component along the C-H bond axis, with $\eta = 0.02$ whereas Tucker and Tomasevich²⁵ obtain values of $q = 0.2426$ and $\eta = 0.04$.

In our calculations the principal EFG axis has been determined in all the three schemes. In the CNDO/2 scheme we get for the angle between the C-H bond and the EFG principal axis a value of 1.3° . In INDO, this angle is changed to 1.6° , while NN-INDO puts the angle as 3.6° in the opposite sense. It is worth noting that all the three semi-empirical MO formalisms used here yield higher q values and very low η values in comparison with experiment.

IV.2.2 Nitrogen Field Gradients

EFG's at the N site in NH_3 and N_2H_4 have been studied in the present work. Our results for these are presented in Table IV.2.

NH_3

The calculated principal EFG axis for the N-centre in ammonia from CNDO/2, INDO and NN-INDO formalisms is found to coincide with the molecular symmetry axis. O'Konski and Ha²⁶ investigated the EFG's at the N site in NH_3 using nine and twelve gaussian lobe group orbitals and obtained theoretical q

values of -1.959 and -1.045, respectively. Eletr et al.²⁷ investigated the effectiveness of one-centre expansion method and obtained results in satisfactory agreement with multi-centre SCF wave functions. Ditchfield et al.²⁸ report values ranging from -1.277 to -1.732 for STO-nG functions with n ranging from 2 to 6. Olympia²⁹ examined Configuration Interaction (CI) effects on the EFG at the N centre in NH_3 using fixed molecular geometry and orbital parameters with a series of one-centre expansions. With a single configuration the q was found to be -0.8133; with CI the value became -0.92951. Dewar et al.³⁰ calculated the EFG in NH_3 but these authors approximated the two- and three-centre integrals and hence their results are not strictly comparable with either our results or ab initio results. Dixon⁹ calculated the EFG in NH_3 , using STO double zeta wave functions as well as various gaussian expansions for STO basis, and obtained a value of -1.315 for the double zeta function and values ranging from -0.602 to -1.281 for the various gaussian expansions. D.A. Zhogolev et al.³¹ used a mixed basis of STO's and gaussians centred on H atoms in their ab initio calculations. Their value for this basis was -1.76, agreeing with the pure STO result of -1.74. Barber, Hayne and Hinchliffe³² have recently obtained an ab initio value of -1.0471. Experimentally the value obtained by Kukolich³³, by molecular beam method for q, is -0.877. The ab initio results cover a wide range of q values while the semi-empirical results are higher than the experimental value. The NN-INDO result is not much different in this case from the CNDO/2

and INDO results. This situation is to be contrasted with the deuterium case.



Arrighini et al.³⁴ using gaussian lobe orbitals calculated a q value of -2.390 and a η value of 0.561. Kochanski, Lehn and Levy³⁵ obtained a q value of -1.56 for the nitrogen field gradient in N₂H₄ along with a η value of 0.3846. Snyder and Basch's⁵ calculation with their double zeta wave functions lead to a q value of -1.2793 and a η value of 0.5351. The recent results of Barber, Hayne and Hinchliffe³² are $q = -1.29$ and $\eta = 0.778$. Harmony and Baron³⁶ from their microwave studies reported a value of $q = -0.9328$ and a η value of 0.064. Coming now to our computed q values, CNDO and INDO values have the positive sign whereas NN-INDO value has the negative sign, and is a definite improvement. Our η values are, however, closer to the microwave data.

IV.2.3 Oxygen Field Gradients

We have examined the EFG's at the ¹⁷O sites in water and formaldehyde. The results are presented in Table IV.3.



The principal component of the EFG tensor has a positive sign in the NN-INDO method, whereas it has a negative sign in CNDO/2 and INDO. Also, the direction of the principal component is found to be perpendicular to the molecular plane in the NN-INDO

Table IV.3

EPG's at O Sites

Molecules	CNDO/2		INDO		NN-INDO	
	q_{zz}	η	q_{zz}	η	q_{zz}	η
H ₂ O	-2.93176	0.62	-2.92281	0.67	2.26314	0.37
H ₂ CO	-2.64430	0.07	-2.50956	0.01	-1.03152	0.85

and parallel to the H-H direction in CNDO/2 and INDO. Snyder and Basch's reported theoretical EFG component values⁵ lead to the ^{17}O principal axis being perpendicular to the molecular plane, but their q value is negative (-2.0487). Aung, Pitzer and Chan³⁷ obtained, using a STO minimal basis set, a q value of -2.616 . Kern and Matcha¹⁶ obtained, using a GTO basis, the values of $q = -1.922$ and $\eta = 0.796$ with vibrational corrections. Dunning³⁸ using a GTO basis set got q values of -1.9711 and -1.9245 using different basis set contractions. Gornostansky and Kern³⁹, using a STO minimal basis set obtained a q value of -2.62 and η value of 0.78 . With STO double zeta basis set Bendazzoli, Dixon and Palmieri⁸ get a q value of -2.288 along with a η value of 0.7928 . Some of the ab initio results have been summarised by Schaefer¹⁹ in his book. For some recent ab initio results we may refer the reader to Dixon⁹. A more recent ab initio calculation on water is that of Rosenberg and Shavitt²⁰. Their values are $q = -1.729$ and $\eta = 0.799$. Using maser beam spectroscopy Verhoeven⁴⁰ et al. obtained an experimental value of -1.6463 for q and a value of 0.75 for η .

At the semi-empirical level ours appears to be the first calculation with the inclusion of all integrals. The CNDO/2 and INDO results predict correctly the sign of q . They also yield a fairly reasonable estimate of η . The performance of NN-INDO, however, is rather disappointing. Whether this is a consequence of the parametrisation or is due to a deep-rooted cause is not clear at this stage.



In all our three calculations based on CNDO/2, INDO and NN-INDO the EFG principal component direction is found to be in the molecular plane and perpendicular to the C = O bond.

Neumann and Moskowitz²² using contracted gaussian basis sets obtained a value of -2.2705 for q and 0.644 for η , with the principal axis perpendicular to the C = O bond. They also commented that the earlier work of Foster and Boys⁴¹ was in error mainly due to the error in geometry. We have also noted that our calculated results are quite sensitive to changes in assumed geometry. Snyder and Basch⁵ obtained a q value of -2.6124 and a η value of 0.467, with the axis of the principal component of EFG lying in the molecular plane and perpendicular to the C = O bond. Ditchfield, Miller and Pople²⁸, using various STO-nG and STO bases obtained values for q ranging from -2.194 to -2.9294, the value for the STO-6G calculation agreeing with the STO result. Their η values range from 0.640 to 0.837, the last referring to the STO calculation. Garrison et al.²³ report a value of -2.302 for q and 0.624 for η . Flygare and Lowe⁴² have obtained from their high resolution microwave, spectroscopic studies a q value of -2.001 and a η value of 0.695. On reviewing the semi-empirical results we see that the q values of CNDO/2 and INDO appear to be better than the NN-INDO value. However, the η value from NN-INDO is superior.

IV. 3 EFG's in Some Cyclic Molecules

We have selected for our study two typical hetero-cycles one containing nitrogen and the other containing oxygen, viz., pyrrole and furan. The EFG results on these molecules are summarised in Tables IV.4 and IV.5 respectively.

Pyrrole

EFG's at the nitrogen site in pyrrole have been studied by Kochanski, Lehn and Levy³⁵ using contracted gaussian functions. Their q value for the nitrogen is -1.40 which corresponds to a QCC of -6.348 MHz using the conversion factor given in Appendix II. The QCC value given by Kochanski et al. is -5.24 MHz since they use a different conversion factor based on the older Q value of ^{14}N . Their calculated η value is 0.109 . Von Niessen et al.⁴³ report, from their *ab initio* study, a q value of -0.8491 and a η of 0.07 . The experimental QCC value from microwave studies⁴⁴ is -2.66 MHz which corresponds to a q value of -0.587 . The η value reported in this study is 0.09 . The performance of all the three semi-empirical formalisms is poor. This is not surprising in view of the fact that even with the *ab initio* approach von Niessen et al. were not able to reproduce the q value. For the hydrogen attached to the N, von Niessen et al. obtained the values $q = 0.3691$, and $\eta = 0.155$; the EFG principal axis for this hydrogen lies along the N-H bond. The α -hydrogen has $q=0.3625$ and $\eta = 0.081$ and the principal EFG component makes an angle

Table IV.4

EPG Parameters for Pyrrole

Site	CNDO/2		INDO		NN-INDO	
	q_{zz}	η	q_{zz}	η	q_{zz}	η
N	-1.58129	0.409	-1.57936	0.399	0.59388	0.968
H(N)	0.37973	0.122	0.38686	0.120	0.52791	0.056
H _{α}	0.41413	0.033	0.42389	0.039	0.45899	0.029
H _{β}	0.40353	0.018	0.41204	0.024	0.44130	0.004

Table IV.5

EFG Parameters for Furan

Site	CNDO/2		INDO		NN=INDO	
	q_{zz}	η	q_{zz}	η	q_{zz}	η
O	1.62241	0.979	1.71467	0.750	-0.92936	0.990
H _{α}	0.43470	0.024	0.44731	0.030	0.48349	0.017
H _{β}	0.42539	0.005	0.43529	0.019	0.45743	0.013

of 0.46° with the C_α -H bond. For the β -hydrogen von Niessen et al. calculate $q = 0.3656$, $\eta = 0.058$ and the angle between EFG principal component and C_β -H bond as 0.12° . In our calculations the principal component of the EFG tensor at the hydrogen attached to the α carbon makes angles of 1.6° , 3.5° and -4.5° respectively, with the C_α -H bond in CNDO/2, INDO and NN-INDO formalisms, while that of the hydrogen attached to the β -carbon makes angles of 5° , 5° and 5.3° respectively with the C_β -H bond in the above three formalisms. As far as the orientation of the principal EFG component at the N site is concerned, it lies perpendicular to the molecular plane in all our calculations.

The agreement between the results of the semi-empirical formalism and von Niessen et al.'s *ab initio* approach in the case of deuterium EFG's is good and is surprising, in view of the failure of the former methods in the case of ^{14}N .

Furan

Von Niessen et al. have been quoted by Moccia and Zandomeneghi⁴⁵ as having obtained from their *ab initio* calculations the values of 0.3584 and 0.3619 for the EFG at D_α and D_β , with asymmetry parameters of 0.073 and 0.053 respectively. For the oxygen centre, to our knowledge, there is only one earlier report⁴⁶ of a calculation but the EFG values from this work not readily available to us for comparisons. The deuterium field

gradients from semi-empirical methods appear to be consistent, viewed in the light of the ab initio results of Von Niessen et al. However, the ^{17}O results do not show the same consistency. The sign of q obtained in NN-INDO for the oxygen site is different from that of CNDO/2 and INDO. Our calculated EFG tensors for deuterium sites in this molecule have their principal component practically in the same direction as that of the corresponding C-D bond.

Before concluding this chapter it may be remarked that while the deuterium EFG's appear to be amenable to theoretical treatment the nitrogen and oxygen EFG's offer a challenge of a high order. We shall now examine in the next chapter a few more systems containing deuterium, nitrogen, oxygen as well as boron.

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CHAPTER V

EFG's AT D,B,N AND O SITES IN SOME MOLECULES

V.1 General

In Chapter III we saw that the EFG at a given nuclear site is largely determined by contributions from that atom and its near neighbours. This qualitative generalisation forms the basis for a search for chemically significant regularities among the EFG's in a number of related systems. With this background in mind we shall examine, in this chapter, the EFG's at the various quadrupolar nuclear sites in the following molecules. These are : C_2D_4 , CD_3CN , CD_3ND_2 , $DCOND_2$, D_2O_2 , $DONO$, B_2D_6 , $B_3N_3D_6$, BF_3 , N_2F_2 , F_2O and F_2O_2 . The geometries of the molecules studied are indicated in Figure V.1. In cases where the EFG's are non-axial we report the asymmetry parameter values as well.

V.2 EFG's at D-Sites

We shall first consider the deuterium EFG's in the series CD_4 , C_2D_4 , C_2D_2 (see Table V.1). The essential distinction as far as the C-D moiety is concerned is the state of hybridisation of the carbon. Methane and acetylene have already been discussed in the previous chapters, but the values are reproduced here to enable an easy comparison along with our ethylene results in Table V.1. Bloor and Maksic¹ obtained for ethylene, by CNDO/2 method, the values $q = 0.413$ and $\eta = 0.029$, which are somewhat different from ours; the difference is probably due to the difference in geometries used. Barfield et al.², using the INDO formalism with Hehre-Stewart-Pople orbital exponents

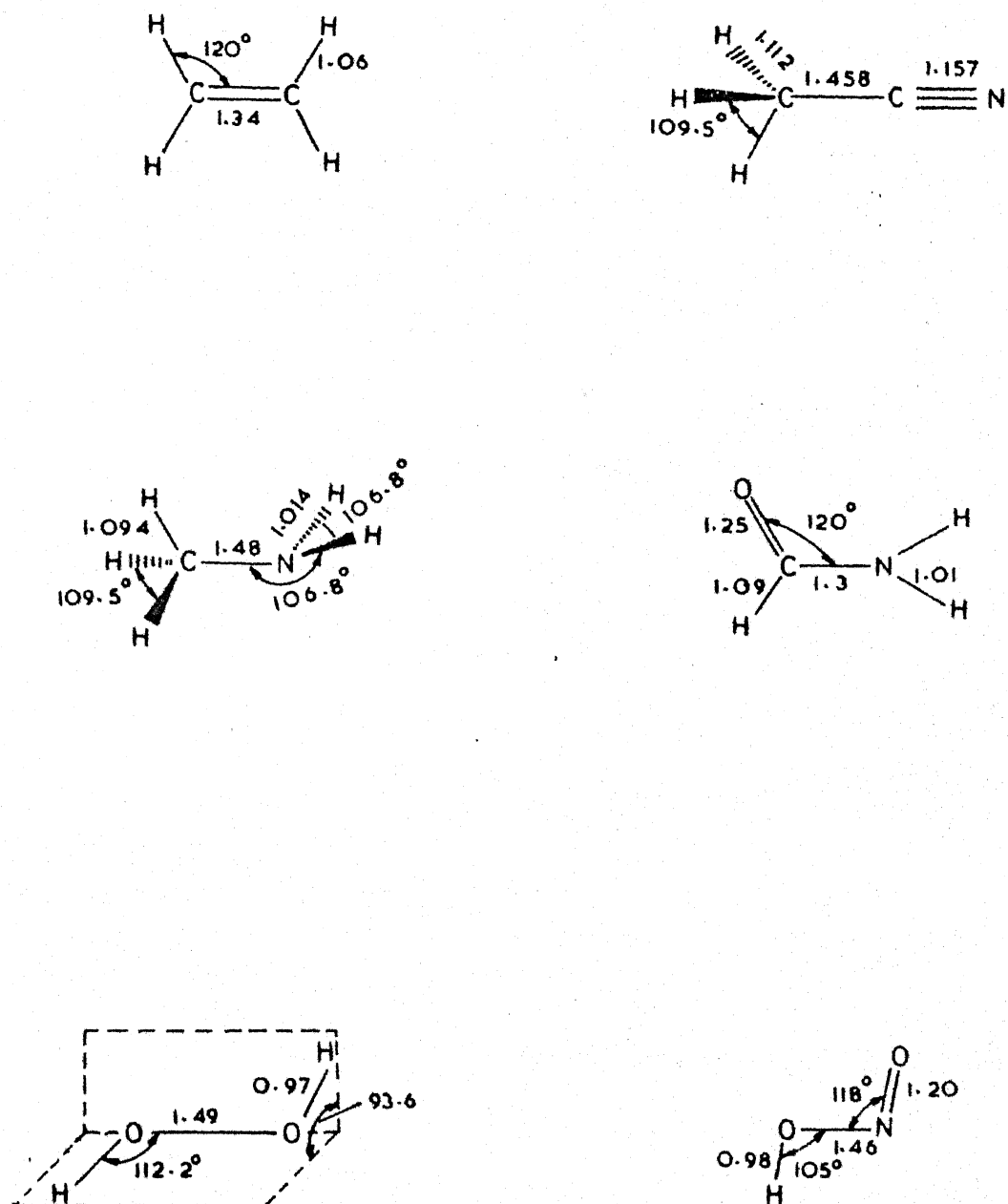


FIG. V-1 (a). GEOMETRY OF THE MOLECULES STUDIED

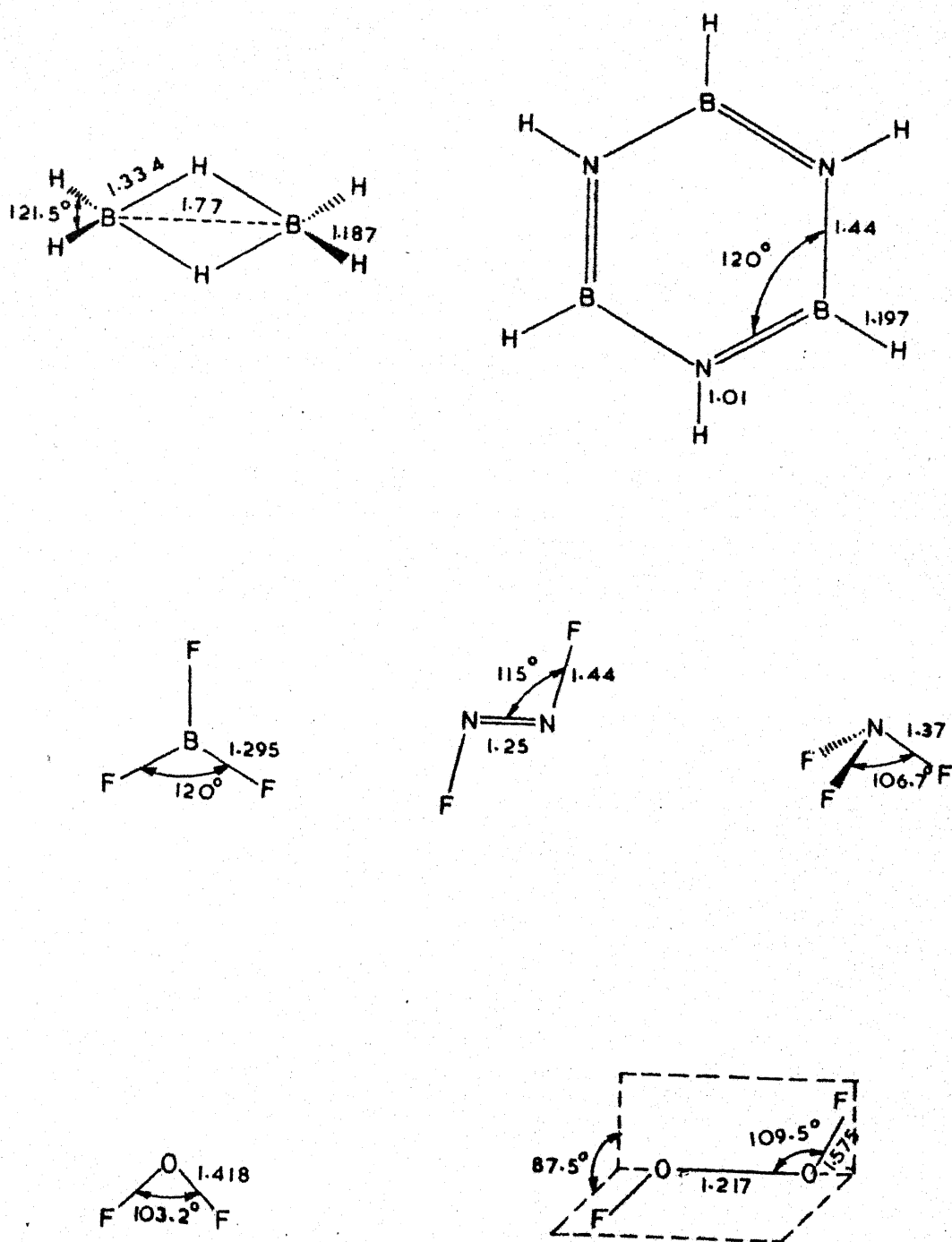


FIG. V.1 (b). GEOMETRY OF THE MOLECULES STUDIED

Table V.1
EFG's at D Sites in CD_4 , C_2D_4 and C_2D_2

Molecule	Method	q	η
CD_4	CNDO/2	0.39608	0.0
	INDO	0.40869	0.0
	NN-INDO	0.53256	0.0
C_2D_4	CNDO/2	0.46846	0.027
	INDO	0.47791	0.033
	NN-INDO	0.59901	0.027
C_2D_2	CNDO/2	0.63291	0.0
	INDO	0.62369	0.0
	NN-INDO	0.53022	0.0

obtained a q value of 0.4468 with $\eta = 0.04$ for ethylene. Calculations at the ab initio level for this molecule have been done by Harrison³ and Schulman et al.⁴, yielding values of $q = 0.3780$ and $q = 0.3188$ respectively. The latter authors obtained a η value of 0.05. Snyder⁵ has reported a value of $q = 0.344$ and $\eta = 0.039$ using double zeta basis set for ethylene.

It is seen clearly that CNDO/2 and INDO methods give q values that decrease along the series $C_2D_2 > C_2D_4 > CD_4$. The same trend can be seen from the ab initio results of Snyder⁵. On the other hand, the NN-INDO results do not show this trend. The exponents used on the carbon atom in the NN-INDO method are the Burns exponents which correspond to a valence state s^1p^3 . It seems likely that due to this choice of exponents, the deuterium q values do not reflect the above trend in the NN-INDO calculations. The η values for ethylene from NN-INDO agree fairly well with that from other methods. We may note here that Rinne, Depireux and Duchesne⁶ had pointed out earlier the dependence of the EFG at the deuterium site in the C-D bond on the state of hybridisation of the carbon. The trend $C_2H_2 > C_2H_4 > CH_4$ noticed here with CNDO/2 and INDO formalisms is in conformity with the work of these authors.

Table V.2 presents our results on the molecules CD_3CN , CD_3NH_2 and $DCONH_2$. Bloor and Maksic¹ report a value of $q = 0.378$ and $\eta = 0$ by the CNDO/2 method for CD_3CN . Our CNDO/2

Table V.2

EFG's at D Sites in CD_3CN , CD_3NH_2 , DCONH_2

Molecule	Method	q	η
CD_3CN	CNDO	0.35576	0.003
	INDO	0.36578	0.000
	NN-INDO	0.48090	0.020
CD_3NH_2	CNDO	0.39520	0.024
	INDO	0.41039	0.022
	NN-INDO	0.52945	0.008
DCONH_2	CNDO	0.43462	0.016
	INDO	0.45222	0.009
	NN-INDO	0.52734	0.010

values are $q = 0.356$ and $\eta = 0.003$. The non-zero η in our calculations is to be noted. Barfield et al.² were able to carry out their calculations on CD_3CN with the inclusion of one- and two-centre integrals only. Their values at this level of approximation with Slater and Hehre-Stewart-Pople exponents are 0.499 and 0.437 respectively with $\eta = 0.05$. Our INDO values with the inclusion of all integrals and with Slater exponents are $q = 0.366$ and $\eta = 0$. The difference between $q = 0.499$ and $q = 0.366$ viz., 0.133 is clearly seen to be the effect of the three-centre integrals. The NN-INDO method yields a higher q value in comparison with CNDO/2 and INDO as in the other deuterium calculations. The asymmetry parameter value is also higher. Snyder⁵ has reported values of $q = 0.309$ and $\eta = 0.049$ from his ab initio studies. Kukolich et al.⁷ have experimentally determined the q value to be 0.249. All the theoretical q values are seen to be higher.

For CD_3NH_2 Harrison³ obtains, using gaussian lobe functions, ab initio q values ranging from 0.3552 to 0.3596 depending on the conformation chosen. Our CNDO/2 and INDO values are in good agreement with these ab initio values. The NN-INDO values are again on the higher side.

For DCONH_2 , Snyder⁵ obtains $q = 0.307$ and $\eta = 0.03$ from his ab initio calculations. Our semi-empirical q values are all higher while η values are lower.

Comparing CD_3CN and CD_3NH_2 , we see that the q value for the D-site in CD_3CN is lower than that in CD_3NH_2 . This trend is maintained in all the three semi-empirical formalisms. We may attribute this effect to the electronegativity of the substituent on the carbon to which the deuterium is attached. It may be recalled that in Chapter III we had analysed the EFG at D-site in DCN and DCCD atomwise and found that the major contribution to the EFG at the deuterium site comes from the carbon attached to the deuterium of interest. Since this is a two-centre contribution it depends on the electron density on that carbon atom. With a reduction in the density at this carbon it is reasonable to expect a reduction in the electronic contribution to the EFG with a consequent increase in the total EFG. This conclusion is further supported by the trend in the q values of DCONH_2 and D_2CO (0.4346 and 0.3643 respectively, from CNDO/2 calculations, for example).

Results for the DOOD and DONO molecules are presented in Table V.3. Snyder⁵ reports the values $q = 0.574$ and $\eta = 0.146$ for DOOD . The values obtained by us from the semi-empirical formalisms are in fair agreement with regard to both q and η . Our calculations on DONO are, we believe, the first to be reported. We find that the EFG at D is greater in DOOD than in DONO consistently in all the three formalisms. The electronegativity effect is clearly reflected here too.

Results for the D-sites in CH_3ND_2 , HCOND_2 and the D attached

Table V.3

EFG's at D Sites in D_2O_2 and DONO

Molecule	Method	q	η
D_2O_2	CNDO/2	0.50794	0.130
	INDO	0.50942	0.267
	NN-INDO	0.69867	0.109
DONO	CNDO/2	0.43034	0.112
	INDO	0.40728	0.120
	NN-INDO	0.56637	0.086

to N in borazine are presented in Table V.4. Between CH_3ND_2 and HCOND_2 , the differences in the q values are small, being in a range that could be accounted for by simple conformational differences alone. The effect of the farther atom is clearly seen to be marginal. Harrison³ has obtained deuterium q values ranging from 0.4598 to 0.4607 for CH_3NHD (depending on the conformation) from his ab initio calculations using gaussian lobe functions. Our values from CNDO/2 and INDO are in excellent agreement with these values. To our knowledge no other EFG calculations on borazine are available. The q and η values obtained by us for the deuterium attached to the nitrogen in this molecule are similar to those obtained earlier for the D-N moiety in other molecules.

Our results on the EFG at D-sites in diborane and borazine (D bonded to B) are presented in Table V.5. A remarkable feature of the EFG's at the deuterium sites in diborane is the fact that the terminal D-site has a positive q value while the bridge D-site has a negative q value. This feature was first noticed by Snyder⁵, who made ab initio calculations on this molecule. Later, Barfield et al.², who performed INDO calculations with the inclusion of all integrals, also noticed this and have commented on it. Our CNDO/2, INDO and NN-INDO results all confirm this feature. The asymmetry parameter predicted for the bridge D-site is higher than that for the terminal D-site. No experimental confirmation of these calculations are available

Table V.4
 EFG's at D Sites in CH_3ND_2 , HCOND_2 and
 Borazine

Molecule	Method	q	η
CH_3ND_2	CNDO/2	0.46674	0.096
	INDO	0.45722	0.106
	NN-INDO	0.67585	0.106
HCOND_2	CNDO/2	0.45529	0.150
	INDO	0.45961	0.148
	NN-INDO	0.67698	0.118
Borazine ($\text{B}_3\text{H}_3\text{N}_3\text{D}_3$)	CNDO/2	0.46204	0.042
	INDO	0.46757	0.044
	NN-INDO	0.59184	0.025

Table V.5

EFG's at D Sites in Diborane and Borazine

Molecule/ Nucleus	Method	q	η
B_2D_6/D_{term}	CNDO/2	0.30627	0.033
	INDO	0.31430	0.027
	NN-INDO	0.32843	0.003
B_2D_6/D_{bridge}	CNDO/2	-0.36880	0.252
	INDO	-0.37186	0.255
	NN-INDO	-0.45930	0.193
Borazine/D ($B_3D_3N_3H_3$)	CNDO/2	0.30199	0.015
	INDO	0.30797	0.007
	NN-INDO	0.20590	0.016

at present. The q values from semi-empirical wave functions are all higher than those from the ab initio calculations of Snyder. The q values for the D-site obtained in borazine and the terminal deuterium in B_2D_6 from the CNDO/2 and INDO formalisms are close to each other, reflecting the sp^2 -hybrid character of the B orbital bonded to D in both cases. However, NN-INDO gives significantly lower q values for borazine. Considering the fact that the NN-INDO method yielded uniformly larger q values at the D-sites in other cases, the situation in borazine appears anomalous.

V.3 EFG's at B-Sites

Our results on the B centres in B_2H_6 , borazine and BF_3 are presented in Table V.6. The q value for the B-site in diborane from the ab initio calculations of Snyder and Basch⁸ is -0.3074 . The η value obtained by them is 0.844. All our semi-empirical calculations yield q values which are lower in magnitude although their sign is in agreement. The asymmetry parameter values obtained from our calculations are also lower. Since no other calculations on the EFG's at the B site in borazine are available for comparison we shall not discuss them further here. In the case of BF_3 , Snyder and Basch⁸ report a q value of 0.2218 and an asymmetry parameter value zero for the B site. Our semi-empirical calculations using the CNDO/2 and INDO formalisms yield q values which are an order of magnitude larger. The NN-INDO results are not available at the time of writing of this

Table V.6

EFG's at B Sites in Diborane, Borazine and
Boron Trifluoride

Molecule	Method	q	η
B_2H_6	CNDO/2	-0.17509	0.433
	INDO	-0.17037	0.311
	NN-INDO	-0.19711	0.064
Borazine	CNDO/2	0.11211	0.332
	INDO	0.08346	0.562
	NN-INDO	-0.16135	0.713
BF_3	CNDO/2	3.39730	0.003
	INDO	3.41369	0.002
	NN-INDO	-	-

thesis. However, judging from the performance of the semi-empirical MO wave functions, against the back drop of the ab initio wave functions, for the prediction of EFG's at boron sites we feel that the parametrisation for the boron atom in these formalisms would require further optimisation.

V.4 EFG's at N-Sites

Our results obtained on the systems CH_3NH_2 , HCONH_2 and CH_3CN are tabulated in Table V.7. The conformation chosen for CH_3NH_2 is the staggered conformation. CNDO/2 and INDO results show an increase of the q (numerical) value from CH_3NH_2 to NCONH_2 , but NN-INDO shows the reverse trend.

For CH_3NH_2 , the ab initio results of O'Konski and Ha⁹ as well as those of Arrighini et al.¹⁰ agree with each other. Their q value is -1.918 and the asymmetry parameter value is 0.177. Our semi-empirical results are in reasonable agreement with these. Our results for formamide also appear to be in reasonable agreement with those of Snyder and Basch⁸. For CH_3CN , our CNDO/2 and INDO results yield low positive q values, while the NN-INDO yields a negative q value. Ab initio results of Snyder and Basch⁸, as well as the recent ones of Barber et al.¹¹, point to a q value of -0.704 and -1.009 respectively. The experimental value quoted in the paper of White and Drago¹² is -0.9283. The NN-INDO seems to fare better than CNDO/2 and INDO in this case.

Table V.7

EFG's at N Sites in CH_3NH_2 , HCONH_2 and CH_3CN

Molecule	Method	q	η
CH_3NH_2	CNDO/2	-1.42210	0.288
	INDO	-1.55330	0.265
	NN-INDO	-1.32682	0.367
HCONH_2	CNDO/2	-1.91015	0.160
	INDO	-1.89174	0.158
	NN-INDO	-1.23845	0.161
CH_3CN	CNDO/2	0.01951	0.000
	INDO	0.10415	0.000
	NN-INDO	-0.39622	0.000

Our results on HONO, N_2F_2 and borazine are tabulated in Table V.8. The field gradients in HONO by the three methods are comparable. A similar situation is obtained for N_2F_2 . The results of Snyder and Basch⁸ lead to a q value of -1.012 and η value of 0.47 in N_2F_2 . The ab initio q value is in good agreement with the NN-INDO result. In borazine, the EFG's at N-site obtained from both CNDO/2 and INDO methods are comparable but the NN-INDO q value is nearly halved. The η value obtained from NN-INDO is also smaller.

V.5 EFG's at O-Sites

The oxygen field gradient parameters for the molecules H_2O_2 , F_2O and F_2O_2 are presented in Table V.9. All the EFG calculations point to uniformly large η values in these molecules. The NN-INDO method gives positive q values in all these three cases whereas the CNDO/2 and INDO methods yield negative q values. Whether this result is due to the differentiation of the p_x , p_y and p_z orbitals in the NN-INDO method or is due to Burns exponents is not clear. Further work is required in order to understand the situation better.

The q values for oxygen in the molecules $HCONH_2$ and HONO (vide Table V.10) obtained from CNDO/2 and INDO methods are comparable. The high asymmetry parameter values for oxygen in $HCONH_2$ and the oxygen bonded to the hydrogen in HONO from CNDO/2 and INDO formalisms is to be noted. On the other hand, the asymmetry parameter values for the terminal oxygen in HONO are

Table V.8

EFG's at N Sites in HONO, N_2F_2 and Borazine

Molecule	Method	q	η
HONO	CNDO/2	-1.01908	0.172
	INDO	-0.94938	0.257
	NN-INDO	-1.10890	0.252
N_2F_2	CNDO/2	-0.81623	0.905
	INDO	-0.80920	0.886
	NN-INDO	-1.15210	0.803
Borazine	CNDO/2	0.91661	0.806
	INDO	0.91360	0.838
	NN-INDO	0.44907	0.159

Table V.9

EFG's at O Site in H_2O_2 , F_2O and F_2O_2

Molecule	Method	q	η
H_2O_2	CNDO/2	-3.14657	0.319
	INDO	-3.17426	0.347
	NN-INDO	2.13108	0.588
F_2O	CNDO/2	-3.58430	0.338
	INDO	-3.69543	0.297
	NN-INDO	2.56464	0.795
F_2O_2	CNDO/2	-3.12794	0.438
	INDO	-3.07326	0.419
	NN-INDO	2.46060	0.521

Table V. 10

EFG's at O Sites in HCONH_2 and HONO

Molecule / Nucleus	Method	q	η
HCONH_2/O	CNDO/2	-2.46681	0.741
	INDO	-2.33154	0.786
	NN-INDO	-0.96476	0.197
HONO/O^*	CNDO/2	-2.73100	0.593
	INDO	-2.62114	0.709
	NN-INDO	1.85059	0.180
HONO^*/O^*	CNDO/2	-2.97278	0.178
	INDO	-2.85957	0.272
	NN-INDO	-1.49687	0.250

lower. The NN-INDO procedure yields q values of opposite signs for the two oxygen sites in HONO. As noted earlier, CNDO/2 and INDO procedures yield results which are close to each other for oxygen EFG's, while the NN-INDO procedure yields results which differ markedly. This implies that the electronic contribution to the EFG is estimated to be very much different in the NN-INDO procedure as compared to the other two procedures. A better picture can be obtained only after detailed ab initio as well as gas-phase experimental ^{17}O EFG results in this class of molecules become available.

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CONCLUDING REMARKS

We have examined in this thesis, the EFG's at the D, Li, B, N and O sites in a variety of molecules using the three semi-empirical MO formalisms: CNDO/2, INDO and NN-INDO. For the deuterium case, since the major contribution to the EFG comes from the atom to which it is bonded, the orbital exponents for the neighbour atom play a very important role. Since the use of Burns exponents results in a more diffuse orbital, the electronic contribution to the EFG at the D-site decreases, and consequently the total EFG increases in comparison with the EFG values obtained with the use of Slater exponents. Using experimental EFG values, at the deuterium sites, it appears that it would be possible to optimise the orbital exponents in semi-empirical formalisms. The EFG at the Li site in LiD calculated by the NN-INDO method is also encouraging. On the other hand, the EFG's at B- and O-sites from the NN-INDO appear to be anomalous. This clearly indicates the need for reparametrisation of the NN-INDO method. The hope that a formalism, as the NN-INDO, which differentiates between, p_x , p_y and p_z orbitals would succeed in predicting the asymmetry parameter values correctly has been belied. The reason for this failure appears to lie in the fact that the behaviour of the p-orbitals near the nucleus is yet to be properly represented.

A close scrutiny of the literature reveals that even ab initio wave functions fail to represent the experimental EFG's correctly. It is well known that, even with carefully optimised minimal basis sets, it is not possible to obtain reliable values of sensitive one-electron properties such as electric field gradients. The goal of most semi-empirical formalisms has been to mimic the ab initio SCF MO results. Parametrisations and approximations have been done with this end in view. It now appears that a different view-point has to be taken with regard to the parametrisation procedures in the semi-empirical schemes as far as prediction of EFG's are concerned. Since a large number of accurate experimental nuclear quadrupole coupling constants are becoming available, the need for developing a reliable and computationally inexpensive semi-empirical procedure with fewer parameters assumes significance.

Since semi-empirical calculations using 'valence only' basis sets cannot take into account Sternheimer effects, the question of shielding/antishielding effects in molecules with respect to the semi-empirical formalisms needs careful scrutiny. It is implicit in all these calculations that Sternheimer corrections are either zero or constant. It might be possible to develop a theoretical model in which the atomic-like core wave functions are made orthogonal to the semi-empirical valence wave functions. Sternheimer shielding calculations can be carried out with such core wave functions, as is done in the case of atoms.

APPENDIX I

A Listing of FORTRAN 10 Program for the Evaluation of EFG Integrals is given in this Appendix. The Program evaluates the Matrix Element of the Diagonal Component of the EFG Operator. Atomic Orbitalwise Contributions to EFG are also output by this Program.

SUBROUTINE CALC(CIN,CX,CY,CZ)

THIS SUBROUTINE TAKES AS INPUT THE M.O. COEFFICIENT MATRIX
AND THE COORDINATES OF THE SITE AT WHICH THE EFG IS DESIRED
AND WRITES ONTO UNIT 1 (DSK: IN THE DECSYSTEM-10)
THE EFG INTEGRALS OVER THE A.O. BASIS
AND THE ELECTRONIC CONTRIBUTION TO q_{zz}

q_{zz}

THROUGH BLANK COMMON THE NO. OF HYDROGENS, TOTAL NO. OF ORBITALS
AND THE NO. OF VALENCE ELECTRONS ARE INPUT
THE COMMON BLOCK /DDD/ PASSES THE ORBITAL EXPONENTS
AND THE COORDINATES OF EACH ORBITAL CENTRE
ARE PASSED VIA COMMON /XYZ/

note: a digit appearing in col.9 as the first non-blank character
of a line in the listing signifies a continuation line

IMPLICIT REAL*8(A-H,O-Z)

COMMON /NH,NVAL

COMMON /JNM/ALF1,ALF2,PSQ(12),ABS0

COMMON /DDD/CAMU(35)

COMMON /XYZ/IDJMMY(35),X(35),Y(35),Z(35)

DIMENSION Q(35,35),PT(12),PX(12),PY(12),PZ(12),SIGMA(12),TAU(12)

1 JLM(12),NCODE(35),TPZ(12)

DIMENSION P(12),RES02(12),RES03(12),RES04(12),RES12(12),

1 RES13(12),RES14(12),RES22(12),RES23(12),RES24(12)

DIMENSION FUN(12),DEN(12),PART(12)

DIMENSION CIN(35,35),TITLE(35),CONT(35)

DATA PI/3.1415926535897962/

DATA PT/0.009219682876640,0.047941371814762,

1 0.115048662902847,0.206341022856691,

2 0.316084250540910,0.437333295744265,

3 0.562666704255734,0.683915749459090,

4 0.793658977143309,0.884951337097153,

5 0.952058628185238,0.990780317123360/

NOTE: The symbol ^ denotes exponentiation

THE FIRST NH ORBITALS ARE TREATED AS 1S ORBITALS

THE REMAINING ARE TREATED AS 2S AND 2P ORBITALS

FOR ANY OTHER FORMAT OF INPUT THE FIRST FEW LINES NEED REWRITING

WRITE(1,111)

FORMAT(1X,///

***** EFG CALCULATION *****///

1 QZZ INTEGRALS OVER A.O.'S')

NOC=NVAL/2

DO 10 I=1,N

DO 10 J=1,N

Q(I,J)=0.00

DO 20 I=1,NH

NCODE(I)=1

NS1=NH+1

DO 40 I=NS1,N,4

NCODE(I)=2

NCODE(I+1)=3

NCODE(I+2)=4

NCODE(I+3)=5

CONTINUE

LOOP OVER PAIRS OF ORBITALS

```

DO 900 IL=1,N
DO 900 JL=1,N
II=IL
JJ=JL
NC1=NCODE(II)
NC2=NCODE(JJ)
IF(NC1.GT.NC2)GO TO 900
ALF1=CAMU(II)
ALF2=CAMU(JJ)
AX=X(II)-X(JJ)
AY=Y(II)-Y(JJ)
AZ=Z(II)-Z(JJ)
ABSQ=AX*AX+AY*AY+AZ*AZ
ACSQ=(X(II)-CX)^2+(Y(II)-CY)^2+(Z(II)-CZ)^2
BCSQ=(X(JJ)-CX)^2+(Y(JJ)-CY)^2+(Z(JJ)-CZ)^2

```

BRANCH FOR 1-CENTRE INTEGRALS

```

IF(ABSQ.LT.1.0-4.AND.ACSQ.LT.1.0-4)GO TO 25
GO TO 30
IF(NC1.NE.NC2)GO TO 29
IF(NC1.LE.2)GO TO 29
IF(NC1.EQ.5) Q(II,JJ)=4.00*ALF1**3/15
IF(NC1.EQ.3.OR.NC1.EQ.4) Q(II,JJ)=-2.00*ALF1**3/15.
GO TO 900
Q(II,JJ)=0.
GO TO 900

```

TWO- AND THREE CENTRE INTEGRAL EVALUATION

```

CONTINUE
CALCULATION OF INTEGRATION PARAMETERS AT QUADRATURE POINTS
DO 60 L=1,12
PX(L)=PT(L)*X(II)+PT(13-L)*X(JJ)-CX
PY(L)=PT(L)*Y(II)+PT(13-L)*Y(JJ)-CY
PZ(L)=PT(L)*Z(II)+PT(13-L)*Z(JJ)-CZ
PSQ(L)=PX(L)*PX(L)+PY(L)*PY(L)+PZ(L)*PZ(L)
TPZ(L)=3.00*PZ(L)*PZ(L)-PSQ(L)
P(L)=DSQR(P(SQ(L)))
PPP=PT(L)*PT(13-L)
PPP=PPP*(-1.5)
PART(L)=PPP
IF(PSQ(L).LT.1.0-20)GO TO 60
SIGMA(L)=PT(L)*PT(13-L)*ABSQ/PSQ(L)
TAU(L)=(ALF1*ALF1/PT(L)+ALF2*ALF2/PT(13-L))*PSQ(L)/4.00
CONTINUE

```

TRANSFERS TO THE APPROPRIATE SEGMENTS DEPENDING ON ORBITALS
 IMMEDIATELY UPON TRANSFER THE J_{nm} FUNCTIONS ARE EVALUATED
 BY CALLING THE SUBROUTINE AJNM WITH APPROPRIATE ARGUMENTS
 AJNM RETURNS THE VALUE OF J_{nm} (W,F,G) IN THE ARRAY RES_{nm}
 $n+1/2, m$

GO TO (51,52,53,54,55),NC1
 GO TO (100,120,140,160,180),NC2
 GO TO (900,200,220,240,260),NC2
 GO TO (900,900,300,320,340),NC2
 GO TO (900,900,900,400,420),NC2
 GO TO (900,900,900,900,500),NC2

15 1S SECTION

CONTINUE
 CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
 DO 109 I=1,12
 ONE=PART(I)*RES02(I)*ALF1*ALF2
 FUN(I)=ONE*TPZ(I)
 CONTINUE
 CALL GAUS12(FUN,AQ)
 Q(II,JJ)=AQ*ALF1**1.5*ALF2**1.5*2.00/(3.00*PI)
 Q(JJ,II)=Q(II,JJ)
 GO TO 900

15 2S

CONTINUE
 CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
 CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
 DO 129 I=1,12
 ONE=PART(I)*RES02(I)*ALF1
 TWO=PART(I)*RES12(I)*ALF1*ALF2*ALF2/PT(13-I)
 FUN(I)=TPZ(I)*(TWO/2.00-ONE)
 CONTINUE
 CALL GAUS12(FUN,AQ)
 Q(II,JJ)=AQ*ALF1**1.5*ALF2**2.5*2.0/3./DSQRT(3.00)/PI
 Q(JJ,II)=Q(II,JJ)
 GO TO 900

15 PX

CONTINUE
 CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
 CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
 CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
 DO 149 I=1,12
 ONE=PART(I)*ALF1*ALF2
 TWO=PT(I)*AX*RES02(I)-PX(I)*RES03(I)
 THREE=-PX(I)*RES12(I)
 FUN(I)=ONE*(TPZ(I)*TWO+THREE)
 CONTINUE
 CALL GAUS12(FUN,AQ)
 Q(II,JJ)=AQ*ALF1**1.5*ALF2**2.5*2.0/3./PI
 Q(JJ,II)=Q(II,JJ)
 GO TO 900

C
C
C

1S PY

160

```
CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
```

```
DO 169 I=1,12
ONE=PART(I)*ALF1*ALF2
TWO=PT(I)*AY*RES02(I)-PY(I)*RES03(I)
THREE=-PY(I)*RES12(I)
FUN(I)=ONE*(TPZ(I)*TWO+THREE)
```

169

```
CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*ALF11.5*ALF22.5*2.0/3./PI
Q(JJ,II)=Q(II,JJ)
GO TO 900
```

C
C
C

1S PZ

180

```
CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
DO 189 I=1,12
ONE=-PZ(I)*RES03(I)+PT(I)*AZ*RES02(I)
TWO=2*PZ(I)*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(ONE*TPZ(I)+TWO)
```

189

```
CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*DSORT(ALF1*ALF2)*ALF1*ALF2*ALF2/PI*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900
```

C
C
C

2S 2S

200

```
CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)
```

DO 209 I=1,12

```
ONE=RES02(I)
TWO=-0.5D0*ALF2*ALF2*RES12(I)/PT(13-I)
THREE=-0.5D0*ALF1*ALF1*RES12(I)/PT(I)
FOUR=0.25D0*(ALF1*ALF2)**2*RES22(I)/(PT(I)*PT(13-I))
FUN(I)=PART(I)*TPZ(I)*(ONE+TWO+THREE+FOUR)
CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5*2./(9.*PI)
Q(JJ,II)=Q(II,JJ)
GO TO 900
```

209

C
C

220

2S PX

CONTINUE

```
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)
```

DO 229 I=1,12

ONE=ALF2*PX(I)*RES03(I)

TWO=-ALF2*PT(I)*AX*RES02(I)

THREE=-0.5*ALF1*ALF1*ALF2*PX(I)*RES13(I)/PT(I)

FOUR=0.5*ALF1*ALF1*ALF2*AX*RES12(I)

REST=ALF2*PX(I)*RES12(I)

1 -0.5*ALF1*ALF1*ALF2/PT(I)*PX(I)*RES22(I)

FUN(I)=PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR)+REST)

229

CONTINUE

CALL GAUS12(FUN,AQ)

Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/(PI*DSQRT(3.D0))*2./3.

Q(JJ,II)=Q(II,JJ)

GO TO 900

C
C

240

2S PY

CONTINUE

```
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)
```

DO 249 I=1,12

ONE=ALF2*PY(I)*RES03(I)

TWO=-ALF2*PT(I)*AY*RES02(I)

THREE=-0.5*ALF1*ALF1*ALF2*PY(I)*RES13(I)/PT(I)

FOUR=0.5*ALF1*ALF1*ALF2*AY*RES12(I)

REST=ALF2*PY(I)*RES12(I)

1 -0.5*ALF1*ALF1*ALF2/PT(I)*PY(I)*RES22(I)

FUN(I)=PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR)+REST)

249

CONTINUE

CALL GAUS12(FUN,AQ)

Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/(PI*DSQRT(3.D0))*2./3.

Q(JJ,II)=Q(II,JJ)

GO TO 900

C
C

260

2S PZ

CONTINUE

```
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)
```

```

DO 269 I=1,12
ONE=ALF2*PZ(I)*RES03(I)
TWO=-ALF2*PT(I)*AZ*RES02(I)
THREE=-0.5*ALF1*ALF1*ALF2/PT(I)*PZ(I)*RES13(I)
FOUR=0.5*ALF1*ALF1*ALF2*AZ*RES12(I)
REST=-2.0*ALF2*PZ(I)*RES12(I)
1 +ALF1*ALF1*ALF2/PT(I)*PZ(I)*RES22(I)
FUN(I)=PART(I)*((ONE+TWO+THREE+FOUR)*TPZ(I)+REST)
269 CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/(PI*DSQRT(3.00))*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

PX PX

```

CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

```

DO 309 I=1,12
ONE=PX(I)*PX(I)*RES04(I)
TWO=-PT(I)*PX(I)*AX*RES03(I)
THREE=0.5*RES12(I)-0.5*RES13(I)
FOUR=PT(13-I)*PX(I)*AX*RES03(I)
FIVE=-PT(I)*PT(13-I)*AX*AX*RES02(I)
REST=
1 -0.5*RES22(I)
2 +2.*PX(I)*PX(I)*RES13(I)
3 -PT(I)*PX(I)*AX*RES12(I)
4 +PT(13-I)*PX(I)*AX*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR+FIVE)+REST)
309 CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

PX PY

```

CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

```

DO 329 I=1,12
ONE=PX(I)*PY(I)*RES04(I)
TWO=-PT(I)*PX(I)*AY*RES03(I)
THREE=PT(13-I)*AX*PY(I)*RES03(I)
FOUR=-PT(I)*PT(13-I)*AX*AY*RES02(I)
REST=2.0*PX(I)*PY(I)*RES13(I)
1 -PT(I)*PX(I)*AY*RES12(I)
2 +PT(13-I)*PY(I)*AX*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR)+REST)
329 CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

PX PZ

```

340 CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

DO 349 I=1,12

```

ONE=PX(I)*PZ(I)*RES04(I)
TWO=-PT(I)*PX(I)*AZ*RES03(I)
THREE=PT(13-I)*PZ(I)*AX*RES03(I)
FOUR=-PT(I)*PT(13-I)*AX*AZ*RES02(I)
REST=-PX(I)*PZ(I)*RES13(I)
1 -2*PT(13-I)*PZ(I)*AX*RES12(I)
2 -PT(I)*PX(I)*AZ*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR)+REST)
349 CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

PY PY

```

400 CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

DO 409 I=1,12

```

ONE=PY(I)*PY(I)*RES04(I)
TWO=-PT(I)*PY(I)*AY*RES03(I)
THREE=0.5*RES12(I)-0.5*RES13(I)

```

```

FOUR=PT(13-I)*PY(I)*AY*RES03(I)
FIVE=-PT(I)*PT(13-I)*AY*AY*RES02(I)
REST=
1 -0.5*RES22(I)
2 +2.*PY(I)*PY(I)*RES13(I)
3 -PT(I)*PY(I)*AY*RES12(I)
4 +PT(13-I)*PY(I)*AY*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR+FIVE)+REST)

```

409

```

CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2./3.
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

C
C
C

PY PZ

420

```

CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

C

```

DO 429 I=1,12
ONE=PY(I)*PZ(I)*RES04(I)
TWO=-PT(I)*PY(I)*AZ*RES03(I)
THREE=PT(13-I)*PZ(I)*AY*RES03(I)
FOUR=-PT(I)*PT(13-I)*AY*AZ*RES02(I)
REST=-PY(I)*PZ(I)*RES13(I)
1 -2*PT(13-I)*PZ(I)*AY*RES12(I)
2 -PT(I)*PY(I)*AZ*RES12(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR)+REST)

```

429

```

CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2/3
Q(JJ,II)=Q(II,JJ)
GO TO 900

```

C
C
C
C

PZ PZ

500

```

CONTINUE
CALL AJNM(0,2,SIGMA,TAU,PT,RES02)
CALL AJNM(0,3,SIGMA,TAU,PT,RES03)
CALL AJNM(0,4,SIGMA,TAU,PT,RES04)
CALL AJNM(1,2,SIGMA,TAU,PT,RES12)
CALL AJNM(1,3,SIGMA,TAU,PT,RES13)
CALL AJNM(2,2,SIGMA,TAU,PT,RES22)

```

```

DO 509 I=1,12
ONE=PZ(I)**2*RES04(I)
TWO=-PT(I)*PZ(I)*AZ*RES03(I)
THREE=PT(13-I)*PZ(I)*AZ*RES03(I)
FOUR=0.5*RES12(I)

```

```

FIVE=-PT(I)*PT(13-I)*AZ*AZ*RES02(I)
REST=RES22(I)+
1 -5.5*PZ(I)*PZ(I)*RES13(I)
2 +2.0*PT(I)*PZ(I)*AZ*RES12(I)
3 -2.0*PT(13-I)*PZ(I)*AZ*RES12(I)
4 +0.5*PSQ(I)*RES13(I)
FUN(I)=ALF1*ALF2*PART(I)*(TPZ(I)*(ONE+TWO+THREE+FOUR+FIVE)
1 +REST)
509 CONTINUE
CALL GAUS12(FUN,AQ)
Q(II,JJ)=AQ*(ALF1*ALF2)**2.5/PI*2./3.
Q(JJ,II)=Q(II,JJ)
900 CONTINUE
901 CONTINUE
DO 143 IO=1,N
143 WRITE(1,144) (Q(IO,JO),JO=1,N)
144 FORMAT(1X,/,12F10.5)
SUM=0.
DO 910 I=1,N
DO 910 J=1,N
DO 910 K=1,NOC
SUM=SUM+CIN(K,I)*CIN(K,J)*Q(I,J)
910 CONTINUE
SUM=-2.00*SUM
WRITE(1,911) SUM
911 FORMAT(////' electronic contribution to Qzz = 'F10.5///)
DO 1025 K=1,N
ORBSUM=0
DO 1024 IDC=1,NOC
ORBSUM=ORBSUM+CIN(IDC,K)^2*Q(K,K)
DO 1023 L=1,N
IF(L.EQ.K) GO TO 1023
ORBSUM=ORBSUM+CIN(IDC,K)*CIN(IDC,L)*Q(K,L)
1023 CONTINUE
CONT(K)=-ORBSUM*2.00
1024 CONTINUE
1025 CONTINUE
WRITE(1,1050)(CONT(I),I=1,N)
1050 FORMAT(////' ORBITALWISE CONTRIBUTIONS TO Qelec '///
1 (12F10.5))
RETURN
END

```

C *****
C SUBROUTINE GAUS12(X,Y)
C
C

TWELVE-POINT GAUSSIAN QUADRATURE
OVER THE INTERVAL [0,1]

IMPLICIT REAL*8(A-H,O-Z)

DIMENSION X(12),CT(12)

DATA CT/0.023587668193256,0.053469662997659,
1 0.080039164271673,0.101583713361533,
2 0.116746268269177,0.124573522906701,
3 0.124573522906701,0.116746268269177,
4 0.101583713361533,0.080039164271673,
5 0.053469662997659,0.023587668193256/

SUM=0

DO 1 I=1,12

SUM=SUM+CT(I)*X(I)

CONTINUE

Y=SUM

RETURN

END

```

C *****
C FUNCTION BESMOD(N,ARG)
C ROUTINE FOR EVALUATING MODIFIED BESSEL FUNCTIONS
C OF A REAL ARGUMENT FOR INTEGRAL ORDERS.
C K0, K1 ARE EVALUATED FROM THEIR SERIES EXPRESSIONS
C HIGHER ORDER FUNCTIONS ARE OBTAINED BY THE RECURSION FORMULA
C
C      (x)=Kn-1(x) + (2n/x)Kn(x)
C      n+1      n-1      n
C
C FOR ARGUMENTS > 2 A POLYNOMIAL APPROXIMATION IS USED
C AND FINALLY THE REDUCED FUNCTION X^N * Kn(X) IS OBTAINED
C THIS IS THE FUNCTION OCCURRING IN THE DEFN. OF Jnm
C
C IMPLICIT REAL*8(A-H,O-Z)
C DIMENSION FUN(10)
C DATA GAMMA,PI2/0.577215664901532,1.5707963267948981/
10 IF(N-1) 10,50,10
   IF(ARG.GT.2.00)GO TO 30
   Z=ARG/2.00
   COEFFT=-GAMMA-ALOG(Z)
   SUM=COEFFT
   FACTOR=1.00
   TERM=COEFFT
   M=0
20 M=M+1
   FACTOR=FACTOR*(Z/DFLOAT(M))**2
   COEFFT=COEFFT+1.00/DFLOAT(M)
   TERM=FACTOR*COEFFT
   SUM=SUM+TERM
   IF(ABS(TERM/SUM).GT.1.0-9)GO TO 20
   GO TO 40
C POLYNOMIAL APPROX FOR ARG > 2 ,ORDER ZERO
30 X=ARG
   TWOBYX=2.00/X
   S1=1.25331414D0-0.7832358D-1*TWOBYX+0.2189568D-1*TWOBYX^2
   1 -0.1062446D-1*TWOBYX^3+0.587872D-2*TWOBYX^4
   2 -0.25154D-2*TWOBYX^5+0.53208D-3*TWOBYX^6
   S1=S1*DEXP(-X)/DSQRT(X)
   SUM=S1
40 IF(N.GT.1)GO TO 50
   BESMOD=SUM
   RETURN
50 IF(ARG.GT.2.00)GO TO 70
   Z=ARG/2.00
   SERIES=(-GAMMA-DLOG(Z)+0.500)*Z
   M=0
   COEFFT=SERIES/Z
   FAC=Z
60 M=M+1
   FAC=FAC*Z**2/DFLOAT(M*(M+1))
   COEFFT=COEFFT+0.500*(1.00/DFLOAT(M)+1.00/(M+1))
   TERM=FAC*COEFFT
   SERIES=SERIES+TERM

```

```

IF(ABS(TERM/SERIES).GT.1.D-9)GO TO 60
RESULT=1.D0/ARG-SERIES
GO TO 80
APPROXIMATION FORMULA FOR ORDER 1 , X > 2 .....
X=ARG
TWBYX=2.D0/X
S2=1.25331414D0+0.23498619D0*TWOBYX
1      -0.3655562D-1*TWOBYX^2+0.1504268D-1*TWOBYX^3
2      -0.780353D-2*TWOBYX^4+0.325614D-2*TWOBYX^5
3      -0.68245D-3*TWOBYX^6
S2=S2*DEXP(-X)/DSQRT(X)
RESULT=S2
80    IF(N.GT.1)GO TO 90
BESMOD=RESULT*ARG
RETURN

RECURSION FORMULA FOR HIGHER ORDERS

90    FUN(1)=SUM
FUN(2)=RESULT
DO 100 I=2,N
FUN(I+1)=2.D0*DFLOAT(I-1)*FUN(I)/ARG + FUN(I-1)
100   CONTINUE
BESMOD=FUN(N+1)*ARG**N
RETURN
END

FUNCTION FACTOR(N)
IF(N)1,2,3
1     RETURN
2     FN=1
GO TO 6
3     FN=1
DO 4 I=1,N
FN=FN*I
4     CONTINUE
6     FACTOR=FN
RETURN
END
*****

```


APPENDIX II

A List of Conversion Factors for EFG's and Quadrupole
Coupling Constants are given in this Appendix.

APPENDIX II

Conversion Factors

$$\text{QCC (in KHz)}^* = 234.97 \times 10^3 \times \text{Q(in barns)} \times \text{q (in a.u.)}$$

Nucleus	Q(in barns)	Conversion factor for EFG (in a.u.) to QCC (in KHz)	Conversion factor for QCC (in KHz) to EFG (in a.u.)
^2H	2.860×10^{-3} (a)	672.0	1.488×10^{-3}
^7Li	-3.660×10^{-2} (b)	-8599.9	-1.1628×10^{-4}
^{10}B	4.099×10^{-2} (c)	9631.4	1.0383×10^{-4}
^{11}B	8.543×10^{-2} (c)	20073.5	4.982×10^{-5}
^{14}N	1.930×10^{-2} (d)	4534.9	2.2051×10^{-4}
^{17}O	-2.630×10^{-2} (e)	-6179.7	-1.618×10^{-4}

* S. Rotherberg and H.F. Schaefer III, J. Chem. Phys., 53, 3012(1970).

(a) R.V. Reid and M.L. Vaida, Phys. Rev., A7, 1841 (1973);
Phys. Rev. Lett., 34, 1064, (1975).

(b) S. Green, Phys. Rev. A4, 251 (1971).

(c) J.E. Rodgers and T.P. Das, Phys. Rev. A12, 353 (1975).

(d) H. Winter and H.J. Andra, Phys. Rev. A21, 581 (1980).

(e) H.P. Kelly, Phys. Rev., 180, 55 (1969).